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MICROBIAL VOLATILIZATION OF SELENIUM AT KESTERSON RESERVOIR

Interim Report
March, 1988

Prepared for the

U.S. Department of Interior
Bureau of Reclamation
2800 Cottage Way
Sacramento, CA 95825

Under

U.S. Bureau of Reclamation
Contract No. 7-FC-20-05240

by

Department of Soil and Environmental Sciences
University of California
Riverside, CA 92521

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AGRICULTURAL EXPERIMENT STATION
DEPARTMENT OF SOIL AND ENVIRONMENTAL SCIENCES

RIVERSIDE, CALIFORNIA 92521

March 11, 1988

Susan E. Hoffman
U.S. Department of the Interior
Bureau of Reclamation
2800 Cottage Way
Sacramento, CA 95825

Dear Susan:

Enclosed please find our Interim Report entitled "MICROBIAL VOLATILIZATION OF SELENIUM AT KESTERSON RESERVOIR". Please feel free to forward this information to any agencies that may have an interest in this project.

Thank you for your support.

Sincerely,

W. T. Frankenberger, Jr.
Associate Professor of Soil Biochemistry

WTF:jt
Encl.

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Attn: Susan E. Hoffman, Program Manager

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W. T. Frankenberger, Jr. and U. Karlson

Department of Soil and Environmental Sciences
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EXECUTIVE SUMMARY

This study involves the initiation of field plot experiments to confirm the applicability of a fungal bioreclamation process in detoxifying seleniferous soils. In the laboratory it was shown that isolated soil fungi could take up selenium salts (SeO_3 and SeO_4) and convert them into methylated species, primarily dimethylselenide (90%) and dimethyldiselenide (10%). Methylated gases are naturally volatilized into the atmosphere. Dimethylselenide has a relatively high LD_{50} (2200 mg kg^{-1} rat; ipr, injection), thus a low toxicity threshold. Edaphic factors were shown to highly influence this transformation including a carbon source, moisture, aeration and activators. Among the carbon sources, pectin was the most active for the methylation reaction in the laboratory. Because fruits are often high in pectin (25 to 35%), we selected orange peel for this experiment. Adequate aeration and moisture are needed because of the obligate aerobic nature of the fungi. However, a high moisture content can slow down this process. Activators such as zinc, nickel or cobalt have been found to enhance this process up to 300%. Nitrogen addition also enhances the methylation reaction.

Field experiments of Kesterson were initiated on July 28, 1987. Two sites were selected, one in pond 4 and the other in pond 11. The soil was rototilled, the subplots were staked out and amendments were applied. The carbon sources included citrus pulp, cattle manure and straw. Some plots were fertilized with ammonium nitrate, ammonium

sulfate and zinc sulfate. Irrigation was applied to just moisten the upper 2 cm of the soil surface.

Selenium volatilization was monitored in the field with an inverted box system. A vacuum connected to a manifold pulled the air above the soil into a scrubbing solution of alkaline peroxide at 2 L min^{-1}. The trapped volatile Se was oxidized to selenate and analyzed by AAS/hydride generation. Recovery of the described system was determined to be 85%. This system was compared to a vented system with an inlet port. The closed box recovered 14% more volatile Se than the vented system.

The emission rates of volatile Se were monitored from October to February, 1987. In comparing treatments, the cattle manure appeared to be the best in pond 11 with high rates of volatile Se in October and November, 1987. The optimum application rates of manure and citrus were also determined along with the optimum C:N ratio of the combination of straw and N fertilizer. The most promising treatment in pond 4 was the combination of citrus and N with an average emission rate of 169 $\mu g\ m^{-2}\ h^{-1}$ from October, 1987 to February, 1988. The highest rate of emission with this treatment was recorded in October at 363 $\mu g\ m^{-2}\ h^{-1}$. The citrus treatment enhanced alkylselenide production over irrigation alone (without carbon) by 3.57X (November), 2.27X (December), 2.45X (January), and 11.3X (February). The cattle manure and straw treatments were less effective than citrus but more than irrigation alone. The average emission rates of background controls ranged from 1.04 to 3.44 $\mu g\ m^{-2}\ h^{-1}$.

A laboratory study was conducted to determine the influence of temperature on the methylation of Se. Determination of dimethylselenide (DMSe) by GC analyses indicated that for every 10°C rise in temperature, the rate of Se volatilization increased 2.60-fold (Q_{10} = 2.60). By adding a C source (galacturonic acid, 2 mg C g^{-1} soil) the rate was increased an additional 2.63-fold.

The diurnal activity of volatile Se production indicated that this microbial transformation was highly dependent on temperature. The peak of volatile Se emission was always detected in mid-afternoon. There was a significant relationship between volatile Se produced and the atmospheric and soil temperature. Diurnal cycling and temperature coefficient data indicates that Se emission rates will be dramatically increased during the spring and summer months with warmer temperatures.

The quality assurance objectives for measurement of soil Se data was expressed in terms of accuracy, precision, completeness, representation, comparability and detection limits. Split samples among UCR and CSUF show excellent agreement in Se content of soil samples obtained from Kesterson. Profile analyses of some plots are reported from 0 to 24". In one plot (53), Se was detected as high as 6.0 mg kg^{-1} at 6 to 12" and 3.14 mg kg^{-1} at 12 to 18". We are very much concerned that soluble Se deep in the profile will move with a rising water table. The inventory Se content (0 to 6") in pond 4 ranged from 10 to 209 mg kg^{-1} (median = 38.5) and in pond 11 (results are incomplete), 1.7 to 8.63 mg kg^{-1} (median = 3.61).

The potential for Se removal by volatilization was shown to be as high as 50% in 4 months in a controlled laboratory study. Repeated soil amendments with a specific carbon source produced sustained bio-methylation rates, with no indication of diminishing returns after time. Low levels of Se contamination tended to produce the highest volatilization percentages, which indicate that there is no minimal Se level threshold, and microbial Se removal will potentially approach zero Se levels.

Inquiries were made to local business establishments near Kesterson that could provide C sources to accelerate this microbial reaction. Among the materials, tomato pomace, melons, citrus peel and cattle manure are readily available. The overall costs of this operation (including carbon, discing and irrigation) for treatment as post-ODP (on-site disposal plan) of 500 acres would be $2-3 million/year. Depending upon the emission rates of Se in the spring and summer months, it is difficult to estimate how long is needed for complete Se removal on site. However, the laboratory work indicates that warm temperatures will enhance this process dramatically.

CHAPTER 1

DESCRIPTION OF FIELD EXPERIMENT

Field experiments at Kesterson commenced on 28 July 1987. In ponds 4 and 11, areas measuring 100 x 100 ft and 150 x 150 ft, respectively, were rototilled until the top 4 to 6 inches were loosened up. Test plots 12 x 12 ft with 8 ft borders were staked out in both ponds (see Figs. 1-1 and 1-2). Soils were sampled for inventory determination on 29 July 1987.

SOIL AMENDMENTS

Amendments were applied according to the following schedule:

29-30 July 1987	Initial application
1 September 1987	Repeat application, except no straw and fertilizers on any of the straw treatments (not decomposed), and 20 lbs of straw to plots 16, 18, 19, 20, 23, 24, 25, 26, 51, 53, 60, 63, and 64 (to increase porosity).
5 October 1987	Third application, all treatments (no fertilizers), except 1/2-rate of straw to straw treatments, no straw to other treatments, no manure to high manure plots 24 and 26.
1-2 December 1987	Fourth application, all treatments (no fertilizers), except straw only to plots 51, 53, 60, 63 and 65 (20 lbs).

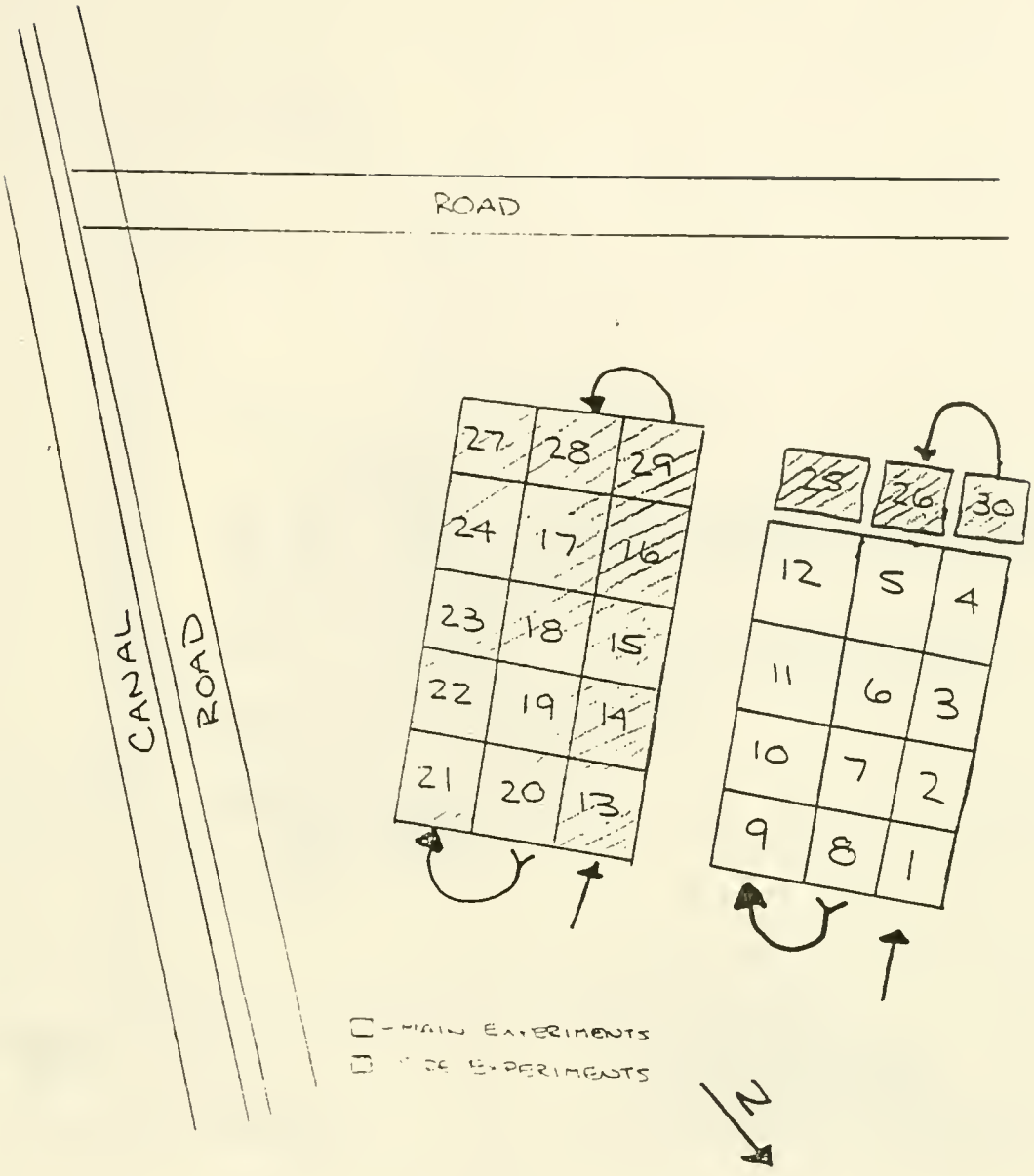


Figure 1-1. Layout of field plots in pond 11.

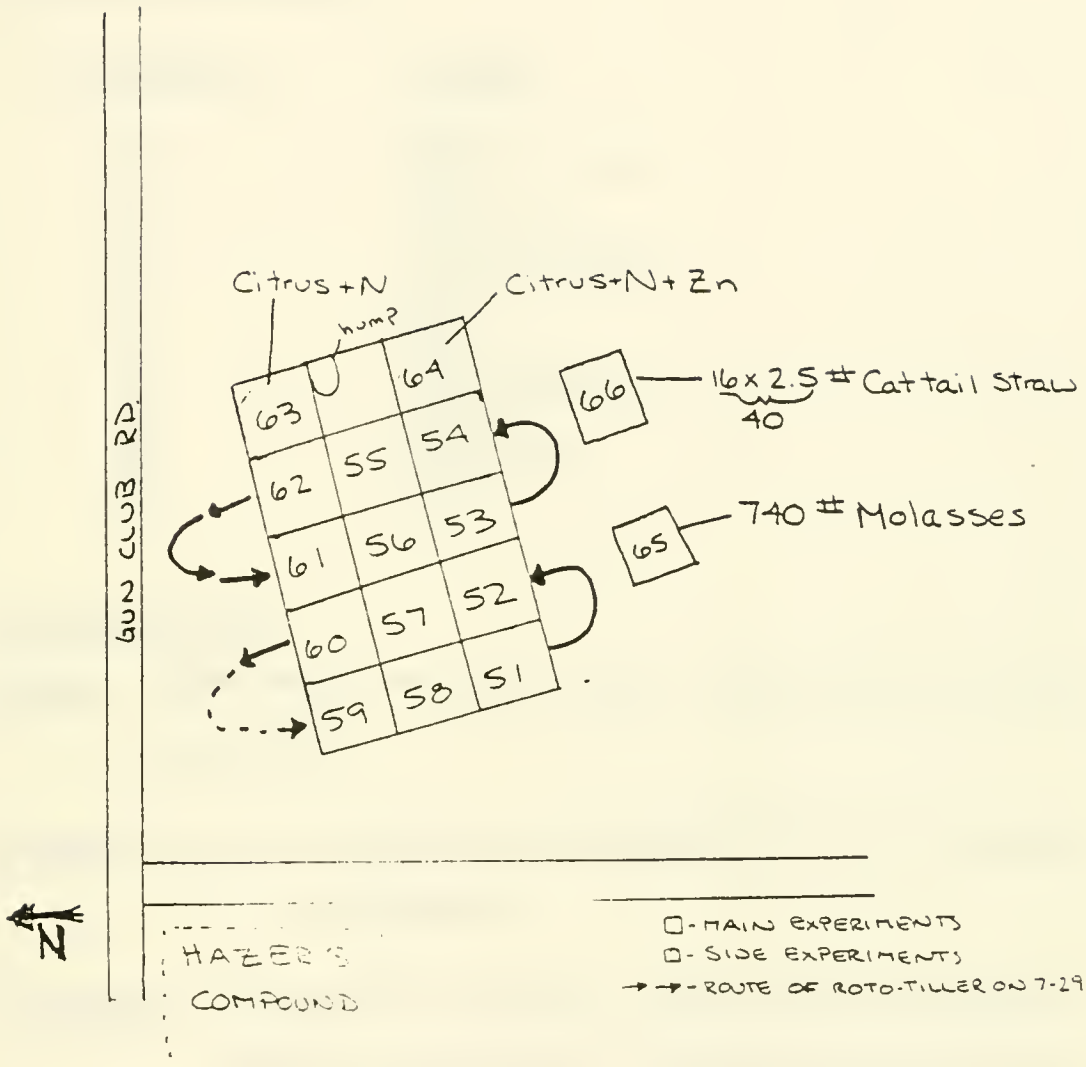


Figure 1-2. Layout of field plots in pond 4.

POND 11 MAIN EXPERIMENTS

Plot number	Treatment
1	Manure
2	Straw (C/N = 10)
3	Manure
4	Citrus pulp
5	Straw (C/N = 10)
6	Moist
7	Moist
8	Citrus pulp
9	Straw (C/N = 10)
10	Manure
11	Citrus pulp
12	Moist

Treatment details:

Manure: cattle manure from Harris feedlot, 10% H_2O. 650 lb (wet wt)/ plot applied

Straw (C/N = 10): wheat straw, dry, chopped, 66.6 lb/plot applied: N, $(NH_4)_2SO_4$

Citrus pulp: orange pulp from Sunkist, Tustin, CA, non-processed; 80% H_2O, crude protein $\geq$ 1.6%, 1000 lb (wet wt)/plot applied

POND 4 MAIN EXPERIMENTS

Plot number	Treatment
51	Manure
52	Straw (C/N = 10)
53	Manure
54	Citrus pulp
55	Straw (C/N = 10)
56	Moist
57	Moist
58	Citrus pulp
59	Straw (C/N = 10)
60	Manure
61	Citrus pulp
62	Moist

Treatment details:

Manure: cattle manure from Harris feedlot, 10% H_2O, 650 lg (wet wt)/ plot applied

Straw (C/N = 10): wheat straw, dry, chopped, 66.6 lb/plot applied; N, $(NH_4)_2SO_4$

Citrus pulp: orange pulp from Sunkist, Tustin, CA, non-processed; 80% H_2O, crude protein $\geq$ 1.6%, 1000 lb (wet wt)/ plot applied

POND 11 SIDE EXPERIMENTS

Plot number	Treatment
13	Citrus pulp + Zn + N
14	Straw (C/N = ∞, no N added)
15	Citrus pulp + N
16	Citrus pulp 300
17	Straw (C/N = 20)
18	Manure 450
19	Manure 300
20	Citrus pulp 450
21	Straw (C/N = 5)
22	Citrus pulp + Zn
23	Citrus pulp 650
24	Manure 1000
25	Citrus pulp 1500
26	Manure 1500
27	Straw (C/N = ∞, no N added)
28	Straw (C/N = 5)
29	Straw (C/N = 20)
30	Moist

Treatment details:

13,15,22	1000 lb (wet wt)/plot orange pulp (80% H_2O) + N [$(NH_4)_2SO_4$] and/or Zn ($ZnSO_4$)
14,17,21,27,28,29	wheat straw, 66.6 lb/plot + N addition to provide C:N ratio of 5 and 20.
16,20,23,25	orange pulp, 80% H_2O: apply 300, 450, 650 and 1500 lb (wet wt)/plot as indicated
18,19,24,26	feedlot cattle manure, 25-30% H_2O (estimated), apply 300, 450, 650, and 1500 lb (wet wt)/plot as indicated

POND 4 SIDE EXPERIMENTS

Plot number	Treatment
63	Citrus pulp + N
64	Citrus pulp + N + Zn
65	Molasses
66	Cattail straw

Treatment details:

63,64 orange pulp (80% H_2O), 1000 lb (wet wt)/plot + N and/or + Zn

65 740 lb molasses/plot, NOT rototilled in originally (too sticky); rototilled starting 25 August 1987

66 40 lb cattail straw, not chopped,. no N addition

ROTOTILLING

All plots were rototilled 4 to 6" deep within 24 hours after application of amendments. In addition, all plots were rototilled on:

13 August 1987

20 August 1987 (pond 4 only)

25 August 1987

After that, once per week.

IRRIGATION

Irrigation started on 30 July 1987. Water quality: Kesterson shallow well water, used through 5 August 1987, EC_e = 11.3 dS m^{-1}; after 5 August 1987, well water from Tracy compound, 0.64 dS m^{-1}.

Irrigation was done daily until 22 October 1987. Water application rates were reviewed and altered periodically. Water quantities were adjusted after visual examination of the top soil with the goal to keep the soil moist but minimize leaching of soil constituents below the 4-inch depth.

IRRIGATION DETAILS:

Date	Change to (daily application, unless noted otherwise)
7/30/87	10 mm, each plot
8/4/87	pond 11: 10 mm, control and manure plots 7 mm, orange pulp plots 7-10 mm, straw plots, individually
	pond 4: 5-9 mm, individually
8/7/87	pond 11: 10 mm pond 4: 7 mm
8/11/87	pond 11: 10 mm pond 7: 3.5-7 mm, individually
8/13/87	pond 4: none
8/14/87	pond 4: 3 mm
8/25/87	switch to sprinkler system, 4 heads per plot
	plot 11: 0.82 mm min^{-1} pond 4: 0.80 mm min^{-1}
	pond 11: 3.3 mm pond 4: 2.4 mm
9/7-8/87	pond 11: none to orange pulp plots, all other plots: 4 min pond 4: 3 min
9/9/87	pond 11: 3 mm (hose) on orange pulp plots
9/26/87	pond 11: turn off south sprinklers every other day on plots 5, 9, 11, 12, 17, 27, 28 pond 4: turn off sprinklers every other day on plots 54, 55 (all) plots 59, 60 (south only)
10/22/87	first rainfall, irrigation omitted when it rained
10/24/87	no irrigation on weekends
10/26/87	flow measurement, pond 11: 42 mL s^{-1} $nozzle^{-1}$
10/26/87	pond 11: 5 min all plots
10/27/87	pond 11: 3 min all plots
11/13/87	heavy rainfall (0.18 inch), irrigation stopped
12/11/87	water ponding on 75% of pond 4

SOIL SAMPLING

A) Profile Sampling

Profiles with subdivisions 0-6 inch, 6-12 inch, 12-18 inch, and 18-24 inch were taken from the center of plots 2, 4, 6, 10, 24, 25, 51-64 on 7/29/87 and on 11/24-25/87. On 1/19/88, samples were taken along the border of plots 59, 63, 65, and 66 to 30" if possible.

B) Surface Sampling

All plots were sampled in a five-point pattern at the 0 to 4 inch depth on:

7/29/87
9/11/87
10/5/87
11/9-10/87
11/30/87
1/14-19/88

CHAPTER 2

MONITORING VOLATILE Se IN THE FIELD

Apparatus

The apparatus used for in-field measurements of DMSe flux is slightly modified from LBL's system. This system consists of a galvanized steel box 22" x 22" x 4" with a brass tubing connector at the top center of the inverted box (Fig. 2-1). The equipment required for this operation consists of a compressor vacuum/pressure pump (Fisher, Tustin, CA), 250 mL gas washing bottles (70 μ porosity) (Fisher, Tustin, CA), 6-place manifold, 1/4" I.D. vinyl tubing, and surgical tubing. Reagents used for the scrubbing solution were H_2O_2 (30%) and 0.05 N NaOH. The purpose of the peroxide was to oxidize the volatile Se into the selenate species.

The soil cover box was placed in the center of each plot to be sampled and pushed into the soil approximately 2". The vacuum pump was connected to an electrical supply near Pond 4 or a generator in Pond 11 and placed in the center of the selected plots to be sampled. The manifold was then connected to the pump with vinyl tubing. A trap was inserted between the manifold and pump to prevent the scrubbing solution from being drawn into the pump in case the gas washing bottle was tipped or blown over by the wind. From the manifold, 6-20 ft sections of vinyl tubing were connected to the sampling boxes. The scrubbing solution consisted of 80 mL 0.05 N NaOH (premeasured) plus 20 mL of H_2O_2 (30%) (final = 6%) which was kept cold in an ice chest. Because vinyl

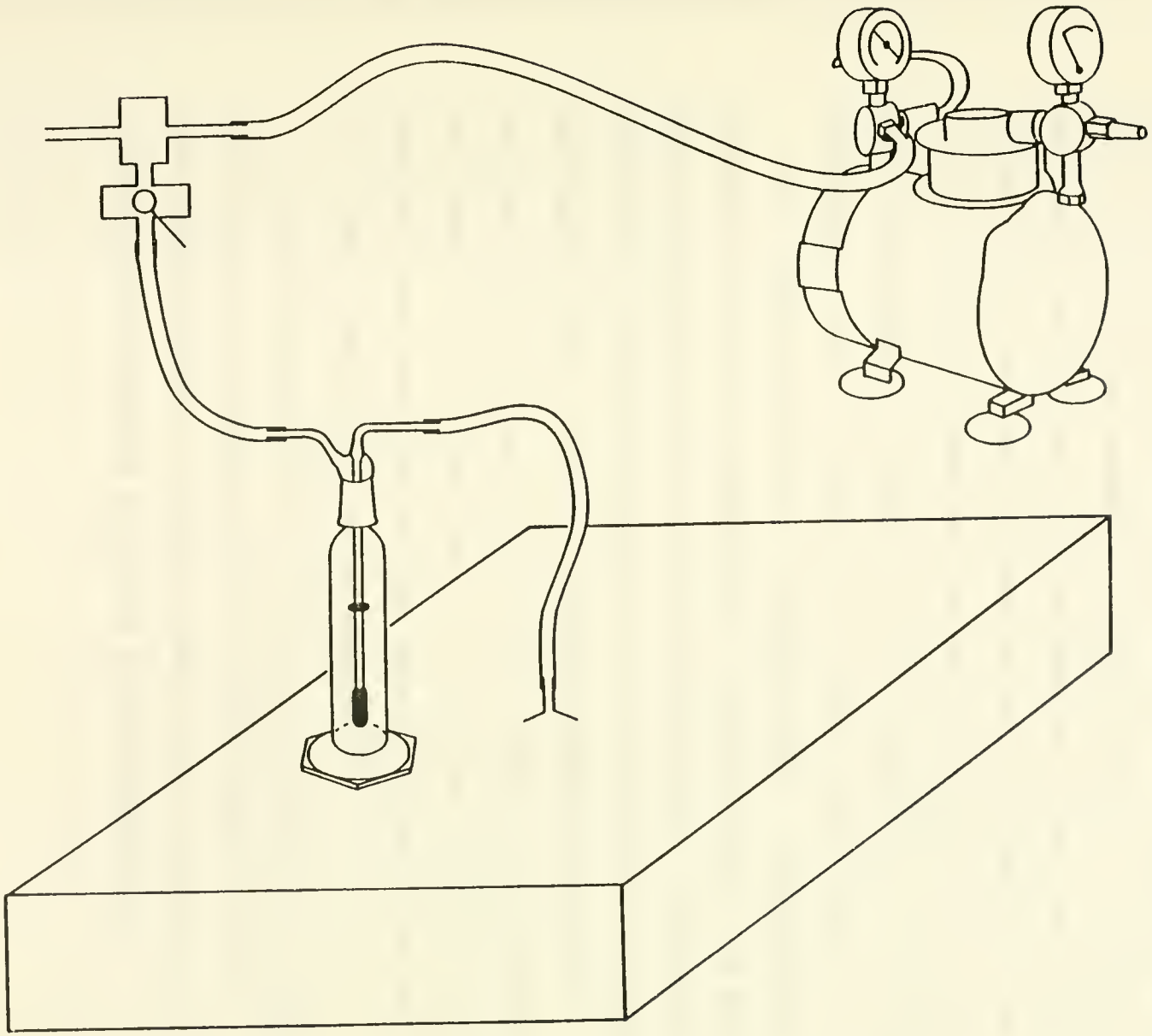


Figure 2-1. Apparatus used to monitor alkylselenide production in the field.

tubing binds to glass and makes it difficult to attach and remove from the washing bottle, a small piece of surgical tubing was placed on the end of the vinyl tubing to alleviate this problem. After H_2O_2 was added and all the tubing was connected, the pump was started. The flow rate of the manifold was adjusted with a flow gauge to 2 L/min. The flow rate was monitored in the field throughout the day during sampling. The duration of the measurements was 1 hr with the starting and finishing times being recorded. Atmospheric and soil temperatures were monitored at the onset and end of sampling and recorded in field logs.

Soil temperature was taken from random plots. A thermometer was inserted into the soil approximately 3" below the surface. The atmospheric temperature was taken inside the inverted box. At the end of the sampling period the pump was turned off and the time and temperatures were again recorded. The washing bottle was opened and the alkali-peroxide solution was poured directly into a 125-mL polyethylene bottle and placed into an ice chest packed with blue ice. The washing bottles were then rinsed twice with deionized water and filled with 80 mL of 0.05 N NaOH to be used for the next sampling.

The alkali-peroxide was boiled to drive off the H_2O_2. A large hot plate with the capacity to hold 12 x 250 mL beakers was used. Each sample was boiled for 15 min, allowed to cool, brought up to volume (100 mL) and poured into 125-mL polyethylene bottles.

Backgrounds and Spikes

Background samples were taken on non-rototilled, nontreated sites adjacent to the plots. Spikes were injected into a glass "U"-shaped tube with a septum on the outside and placed under one side of the sample box with soil packed around it. With a syringe, 0.2 mL of 0.1 mg/mL of DMSe-Se was injected into this tube. Spikes were injected within 5 min of the start of the 1-hr sampling period.

Shipping Samples

All samples were refrigerated (4°C) overnight before shipping. They were placed in an ice chest with several blue ice packs and either shipped by next-day delivery, U.S. mail, or driven to Riverside by David Thomason. The samples were then immediately placed into a cold room at 4°C. The chain-of-custody records were signed upon receipt of samples.

Analyses

Solutions were analyzed for total Se at UCR by taking a 25-mL aliquot into a 50-mL graduate test tube and adding 25 mL concentrated HCl (final concentration = 6 N HCl). The samples were then boiled for 1 hr, allowed to cool and brought to volume with 6 N HCl. The Se content was analyzed by AAS/hydride generation on a Varian Spectra-10 ABQ single beam AA spectrophotometer. Results were reported in volatile emission rates expressed in $\mu g\ m^{-2}\ hr^{-1}$.

Method Development

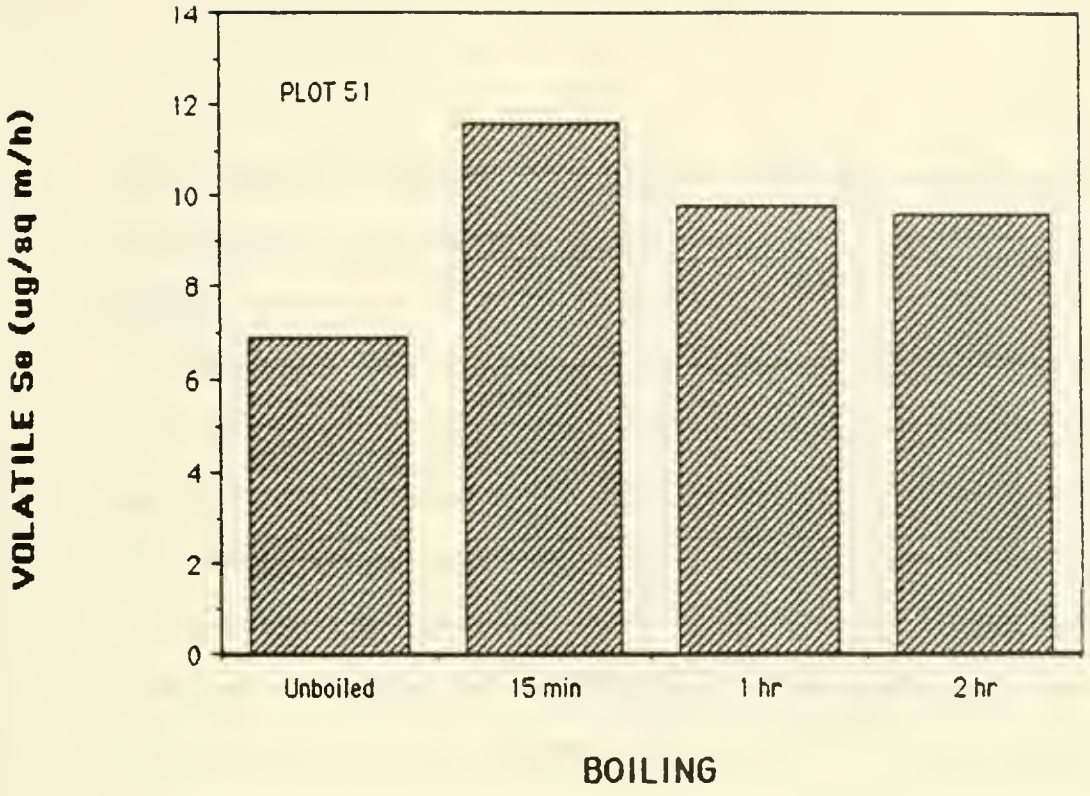
Boiling: Preliminary tests were performed to determine the time required to boil samples for reduction with HCl. Fig. 2-2 illustrates that 15 min of boiling is sufficient when compared to one or two hours. However, unboiled samples resulted in low recovery, ranging from 67-70% to that of boiled samples.

In another preliminary study, the Se content was determined in samples that were boiled, and then allowed to set for 24 h before being analyzed again. Among 10 samples, the average Se content after 24 h from boiling was only 37% of those boiled samples. The range of recovery was 8 to 63%. It is highly recommended that the samples be analyzed by AAS immediately after boiling.

Recovery:

The recovery of the alkaline peroxide sampling system was tested in 2 stages:

1) Recovery of the trap itself: Alkaline H_2O_2 traps were operated as in the field, except detached from the sampling chamber. In place of the sampling box, a 3-inch length of 1/2-inch latex tubing with an air-intake valve was connected to the intake tubing of the trap. The length of the intake tubing was varied between 0 and 2.5 feet. Air-flow rates were adjusted with the valve to 0.5, 1.0, 1.5, 2.0, and 3.0 L min^{-1}. Dimethylselenide (DMSe) standards were injected through the latex tubing



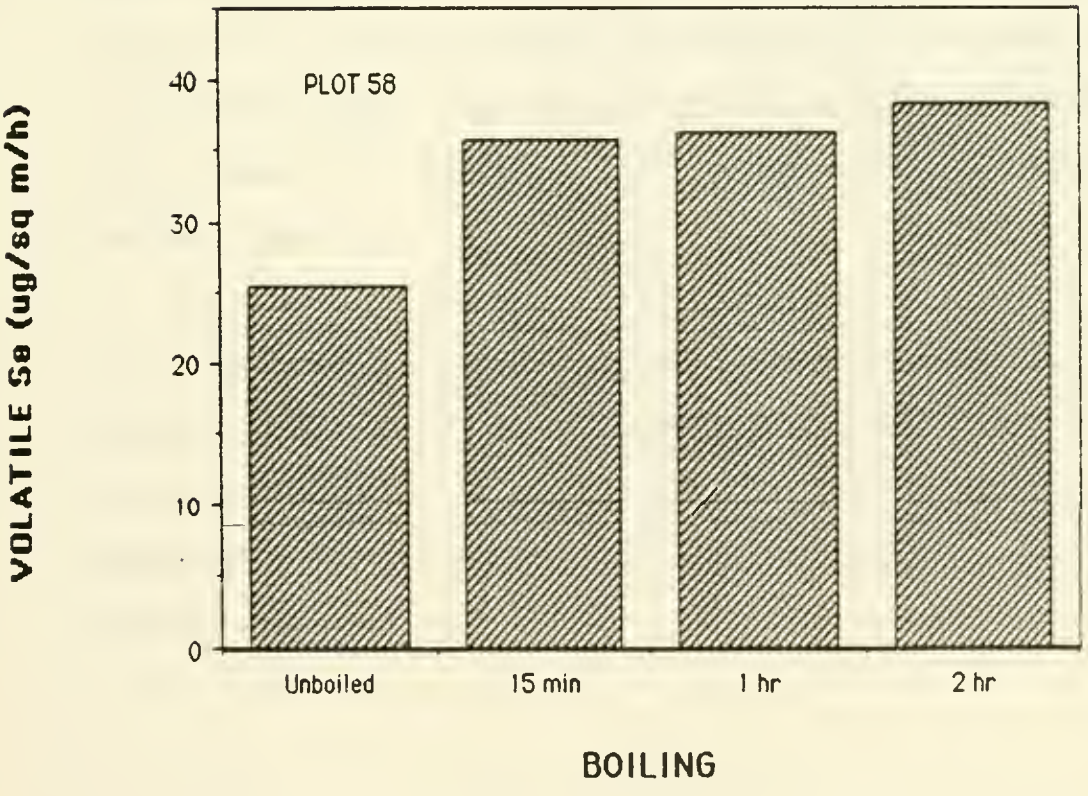


Fig. 2-2. Effect of time of duration in boiling for reduction of Se.

using a gas-tight syringe with a valve. DMSe gas standards were prepared by weighing liquid DMSe into a 10-L glass bottle stoppered with a Mininert septum.

Equivalent DMSe volumes of 2 to 150 μg Se (representing 6.5 to 500 μg m^{-2} h^{-1} volatilization in the field, assuming 100% recovery and 1-hr sampling) were applied in duplicates and at the different flow rates. Traps were analyzed according to the previously described procedure.

Recovery was independent of tubing length and of Se quantity. It was only slightly, but insignificantly, dependent on flow rate. The highest recovery was achieved at 2.0 L min^{-1} and was 85.6 $\pm$ 4.4% (Fig. 2-3).

2) Recovery of the whole system: Sampling devices were operated under field conditions at an air-flow of 2 L min^{-1} on soil known to be free of Se. Fifty μg of DMSe-Se were injected into the sampling chambers via a rubber septum. Traps were analyzed according to standard procedure. Recovery was 18.4 $\pm$ 2.1% (21.5% of the recovery achieved with the trap itself).

The established recovery of the H_2O_2 traps allows for the use of a conversion factor (1/0.856) to convert field measurements into "Se evolved". The surprisingly low recovery of the whole system is not explained sufficiently. It could be due to a number of reasons, including adsorption of DMSe to the soil surface or the interior surface of the sampling chamber.

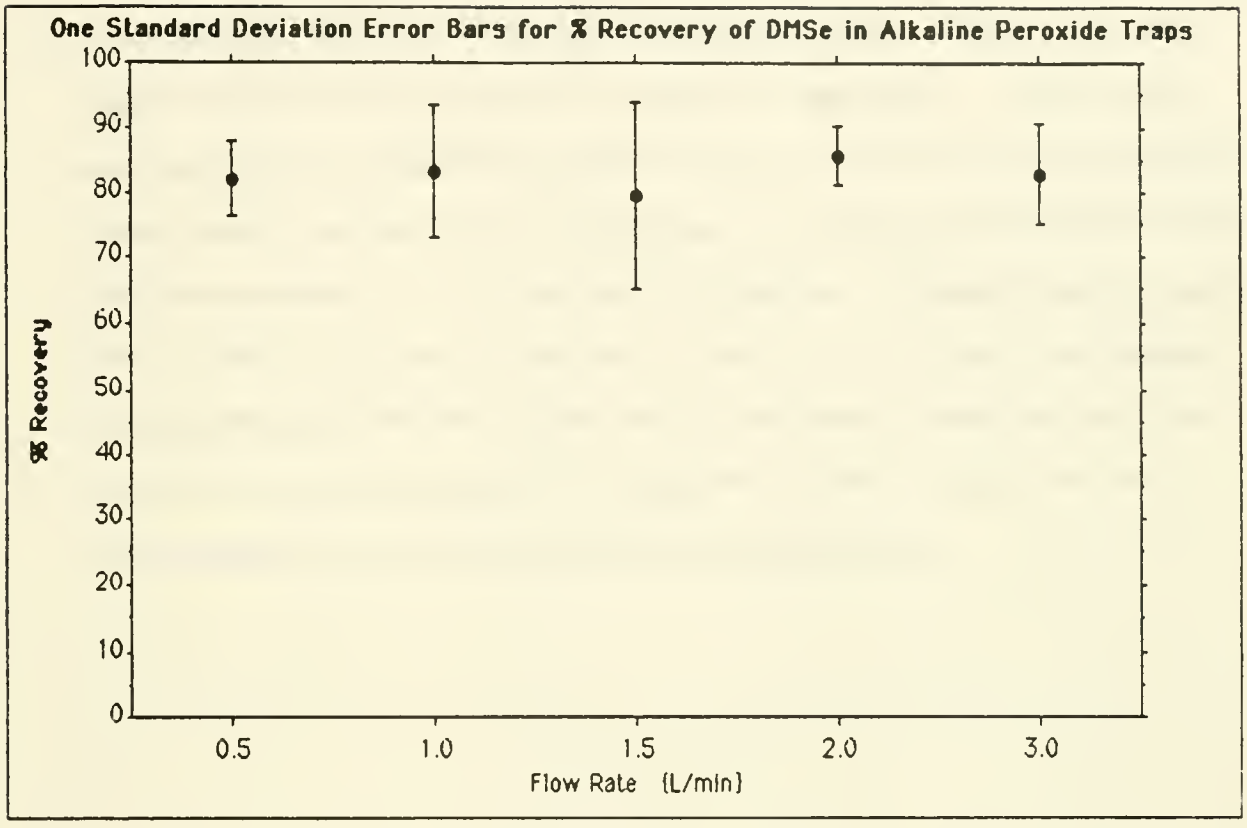


Figure 2-3. Percent recovery of dimethylselenide in alkaline-peroxide traps.

Open vs. Closed Soil Cover Boxes: Tests were made to compare the field measurement of DMSe flux in closed systems vs. an open system with an inlet port in which air sweeps across the surface of the soil. Air most likely enters the closed box around its periphery. Vented boxes were constructed by drilling a hole in the center of one side of the box approximately one inch from the top edge. An inlet port was made with 1/2" PVC pipe attached to a 2' pipe with a 90° elbow. Threaded couplings were used to attach the port to the box. A rubber "O" ring was used between the coupling and box for a tight seal. The results indicate that the vented box recovered approximately 86% of that of a closed cover box. Further sampling will be conducted with vented boxes.

CHAPTER 3

VOLATILE EMISSION RATES OF SELENIUM IN THE FIELD

Pond 11

Emanation of volatile Se was monitored in the field and illustrated in the form of histograms. In August of 1987, LBL reported emission rates ($\mu g\ m^{-2}\ h^{-1}$) of volatile Se among the following treatments: control (29), straw (27), cattle manure (47) and citrus (48). During the cooler months of October and November of 1987, cattle manure appeared to be the best overall treatment resulting in an average emission rate of 9.8 $\mu g\ m^{-2}\ h^{-1}$ (Figs. 3-1, 3-2). These emission rates were much greater than that observed with the moist treatment alone. The manure treatment was also 2-3 times more effective than all of the other treatments tested. The absolute numbers of volatile Se detected was highly influenced by the atmospheric temperature. When the temperatures began to cool (<15°C) (December, January, February), the influence of C materials had little influence on the rates of volatile Se detected in the field (Figs. 3-3 to 3-5).

A study on the application rates of straw indicated that during the months of October, November and February, a C:N ratio = 5 was the optimum to promote alkylselenide production while little influence among the C:N ratios was observed in December (Figs. 3-6 to 3-10). The January data indicates the highest rate of Se emission with C:N = 10.

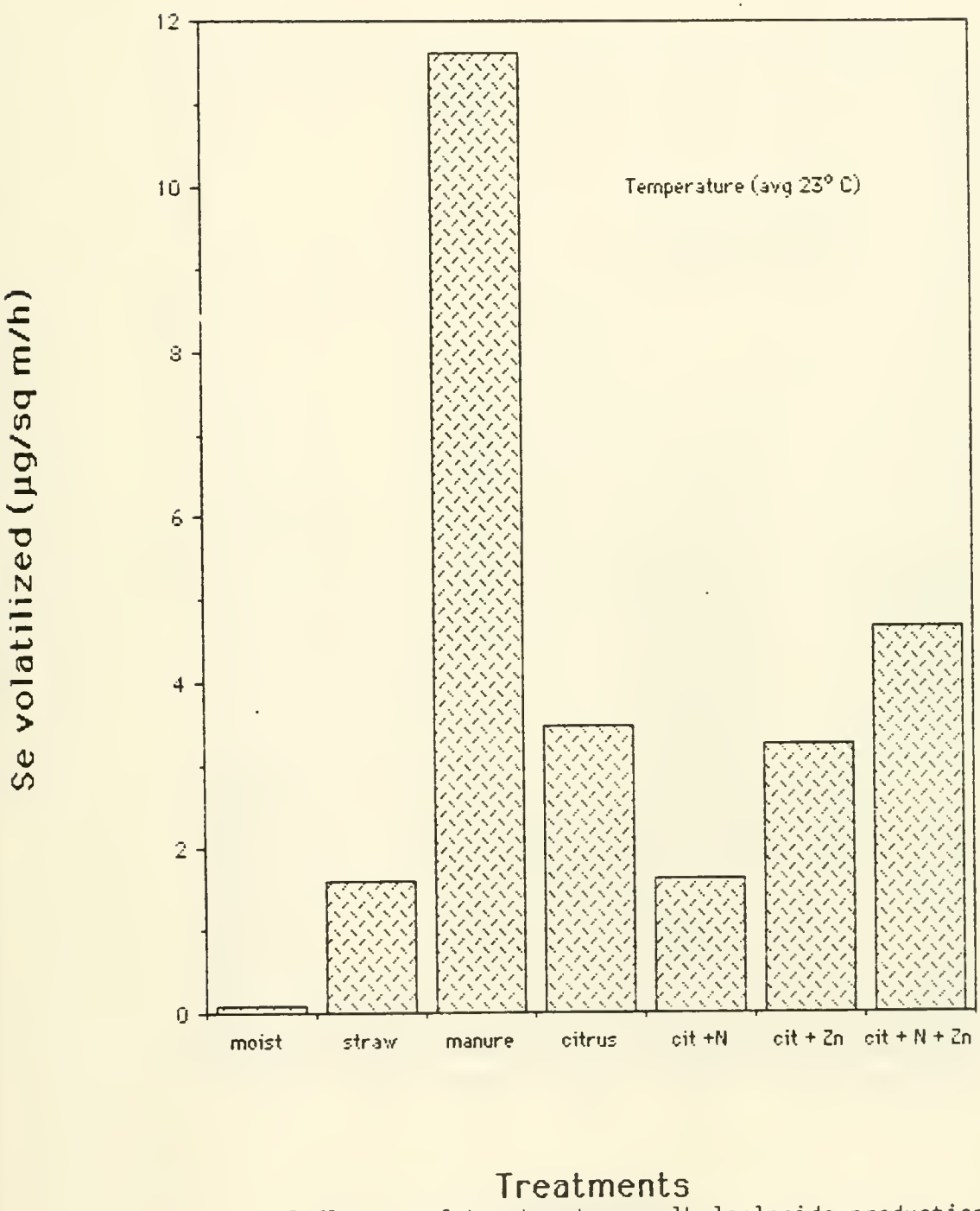


Fig. 3-1. Influence of treatments on alkylselenide production in pond 11 during October 1987.

Fig. 3-2. Influence of treatments on alkylselenide production in pond 11 during November 1987.

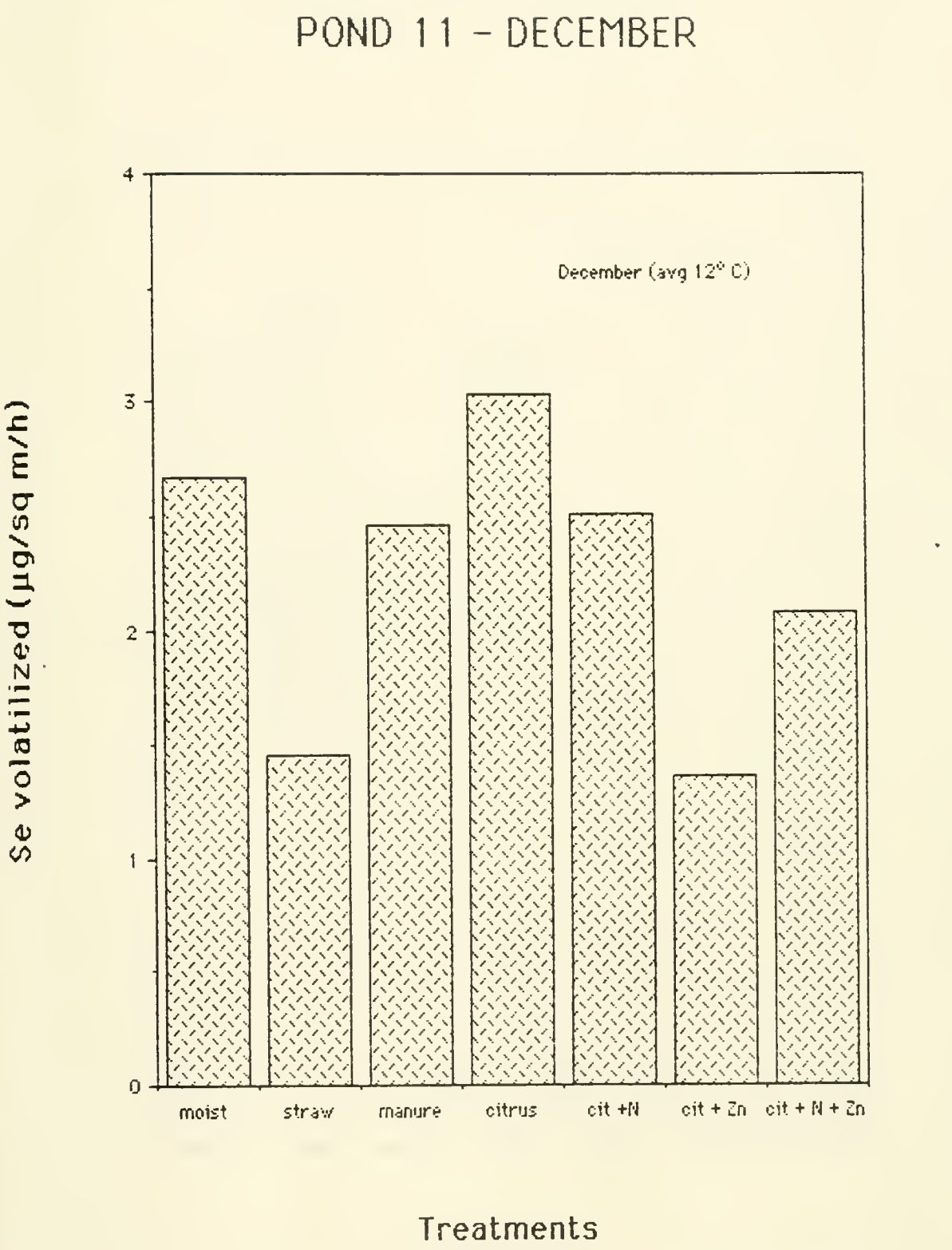


Fig. 3-3. Influence of treatments on alkylselenide production in pond 11 during December 1987.

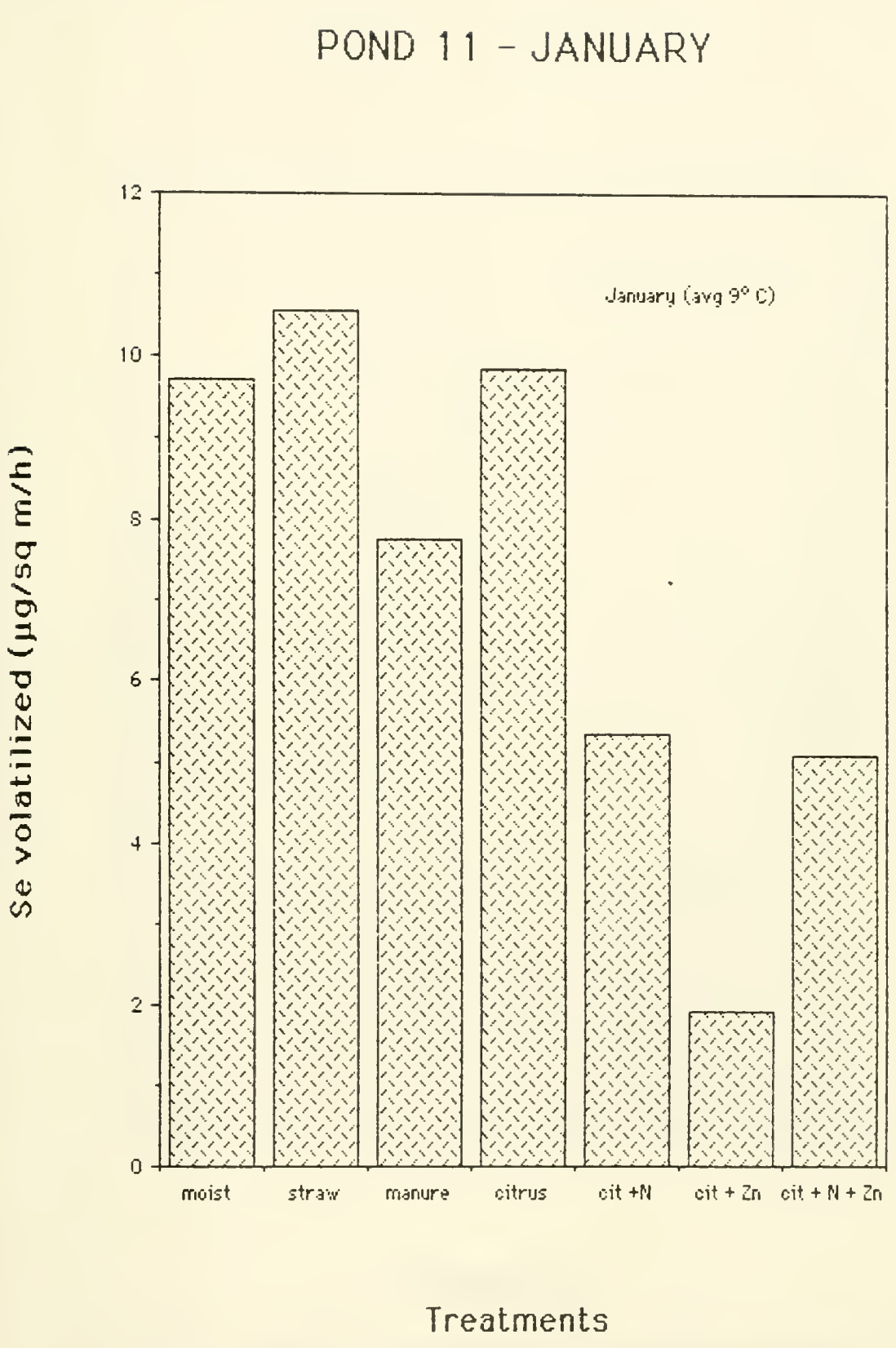


Fig. 3-4. Influence of treatments on alkylselenide production in pond 11 during January 1988.

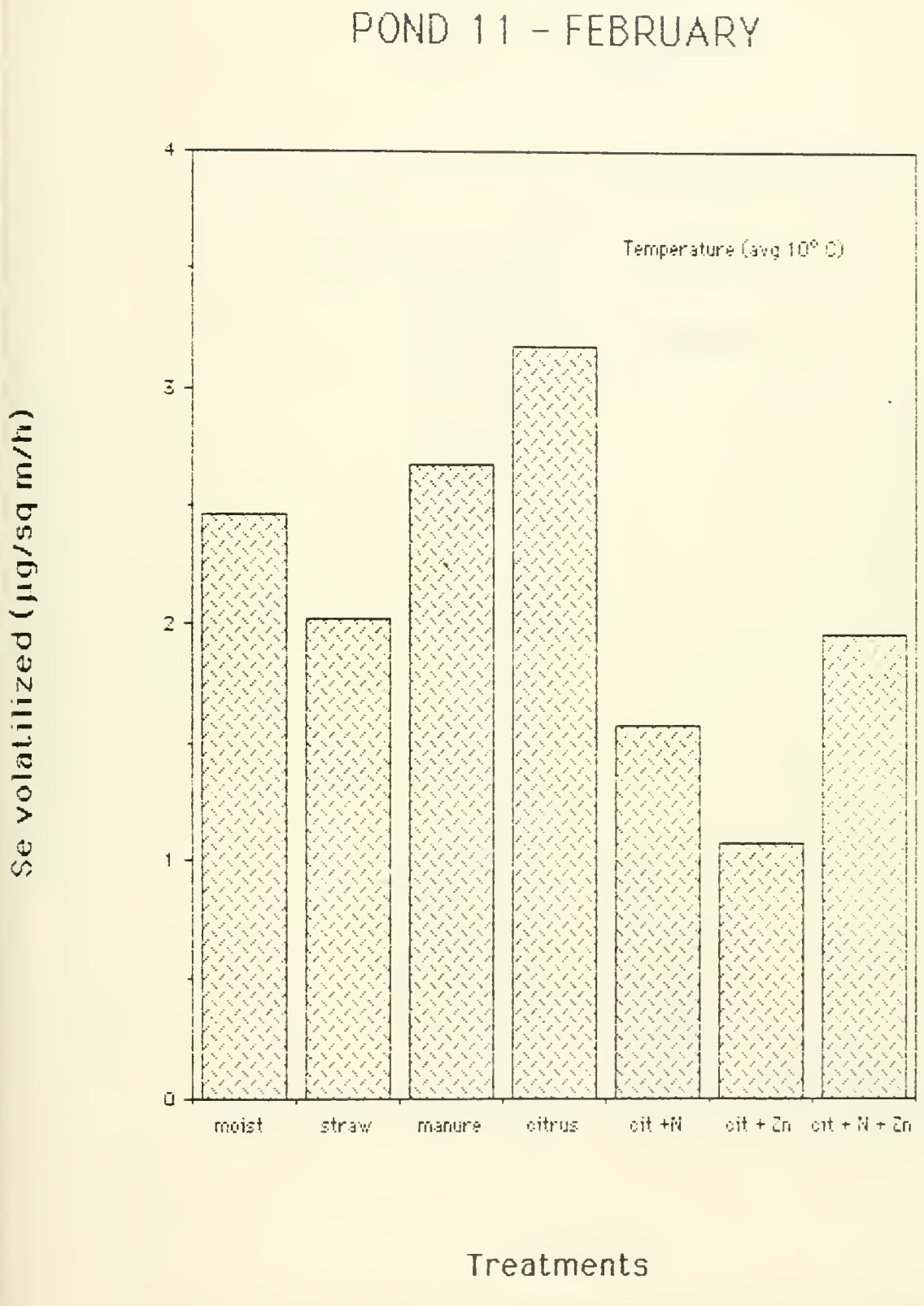


Fig. 3-5. Influence of treatments on alkylselenide production in pond 11 during February 1988.

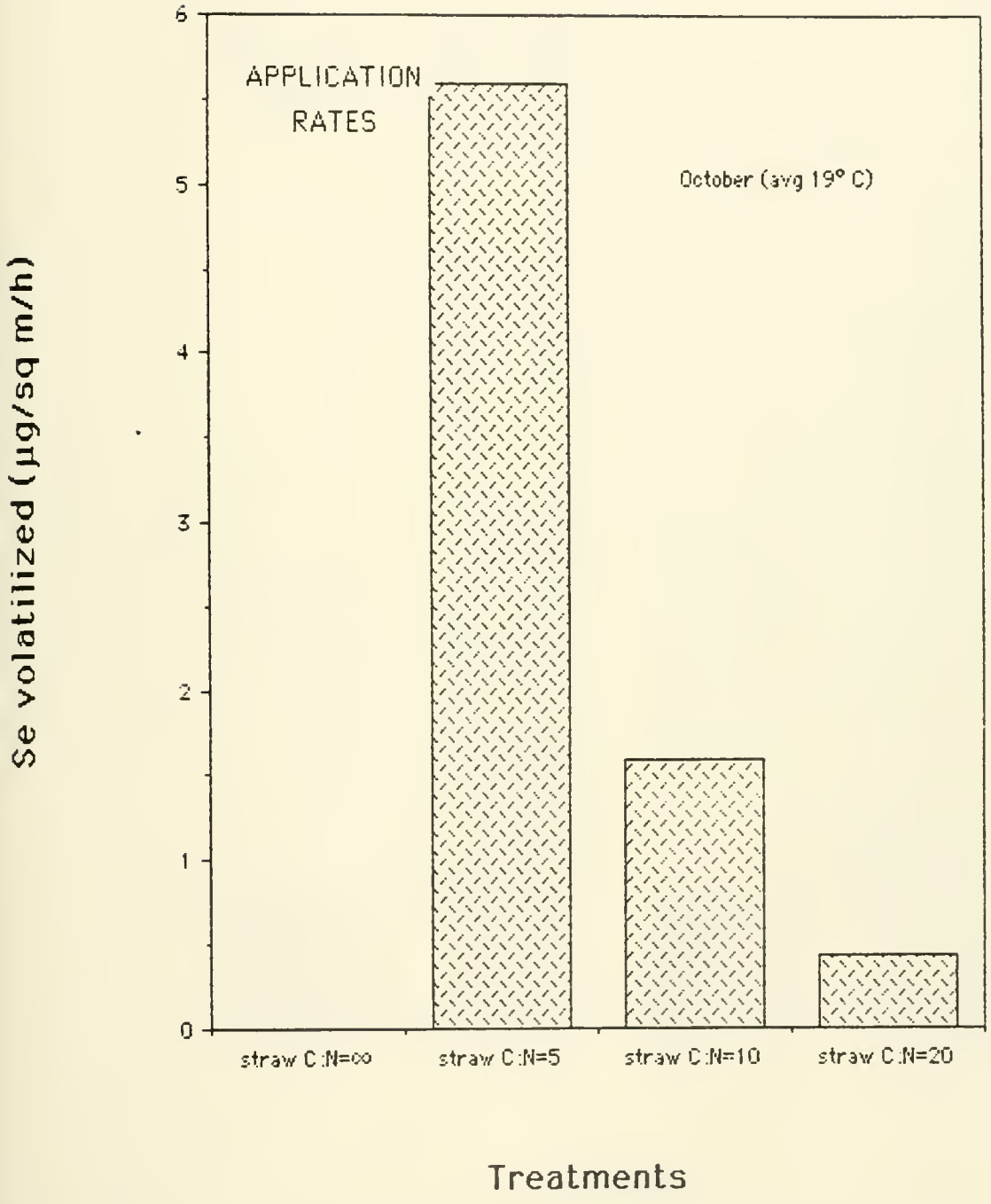


Fig. 3-6. Influence of application rates of straw on alkylselenide production in pond 11 during October 1987.

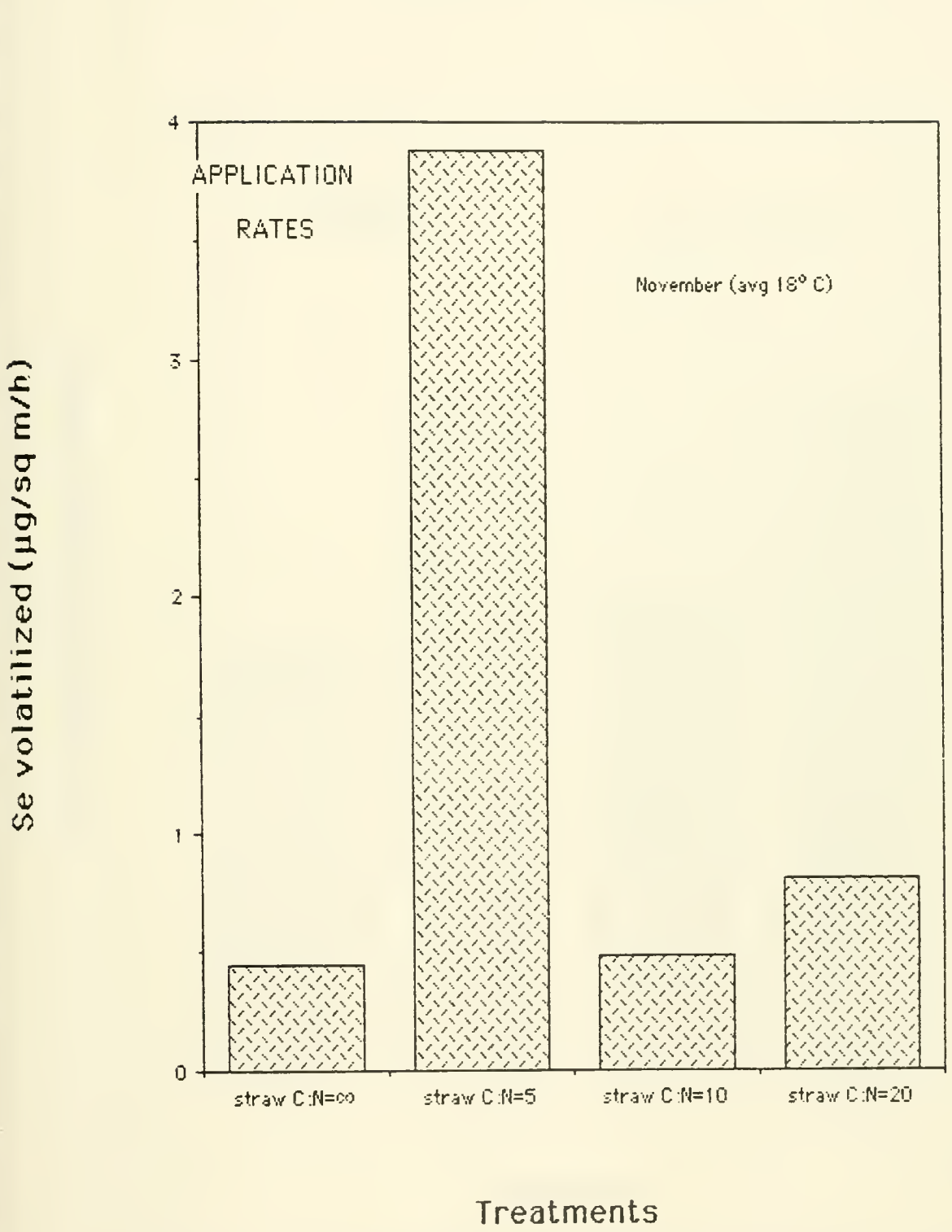


Fig. 3-7. Influence of application rates of straw on alkylselenide production in pond 11 during November 1987.

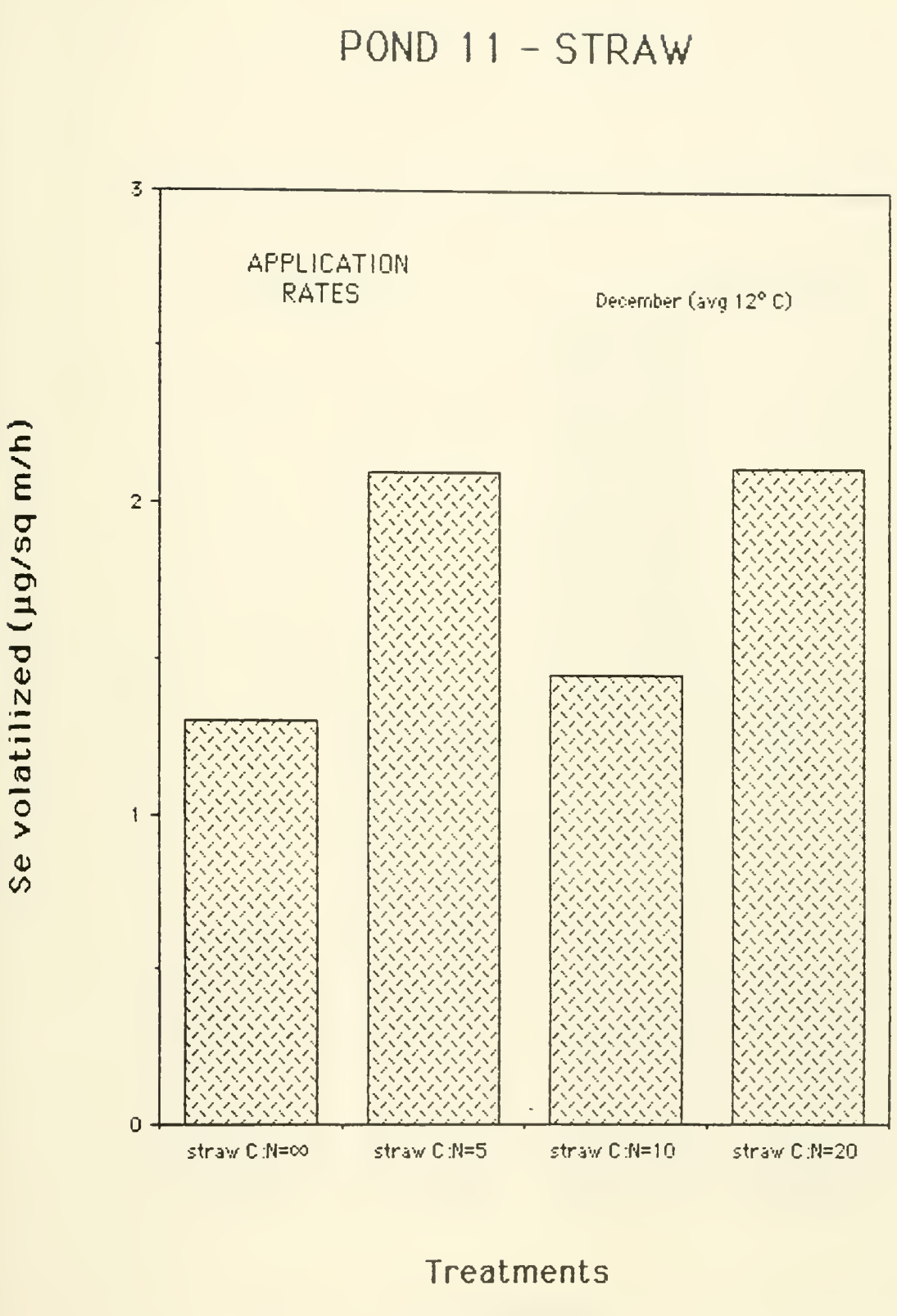


Fig. 3-8. Influence of application rates of straw on alkylselenide production in pond 11 during December 1987.

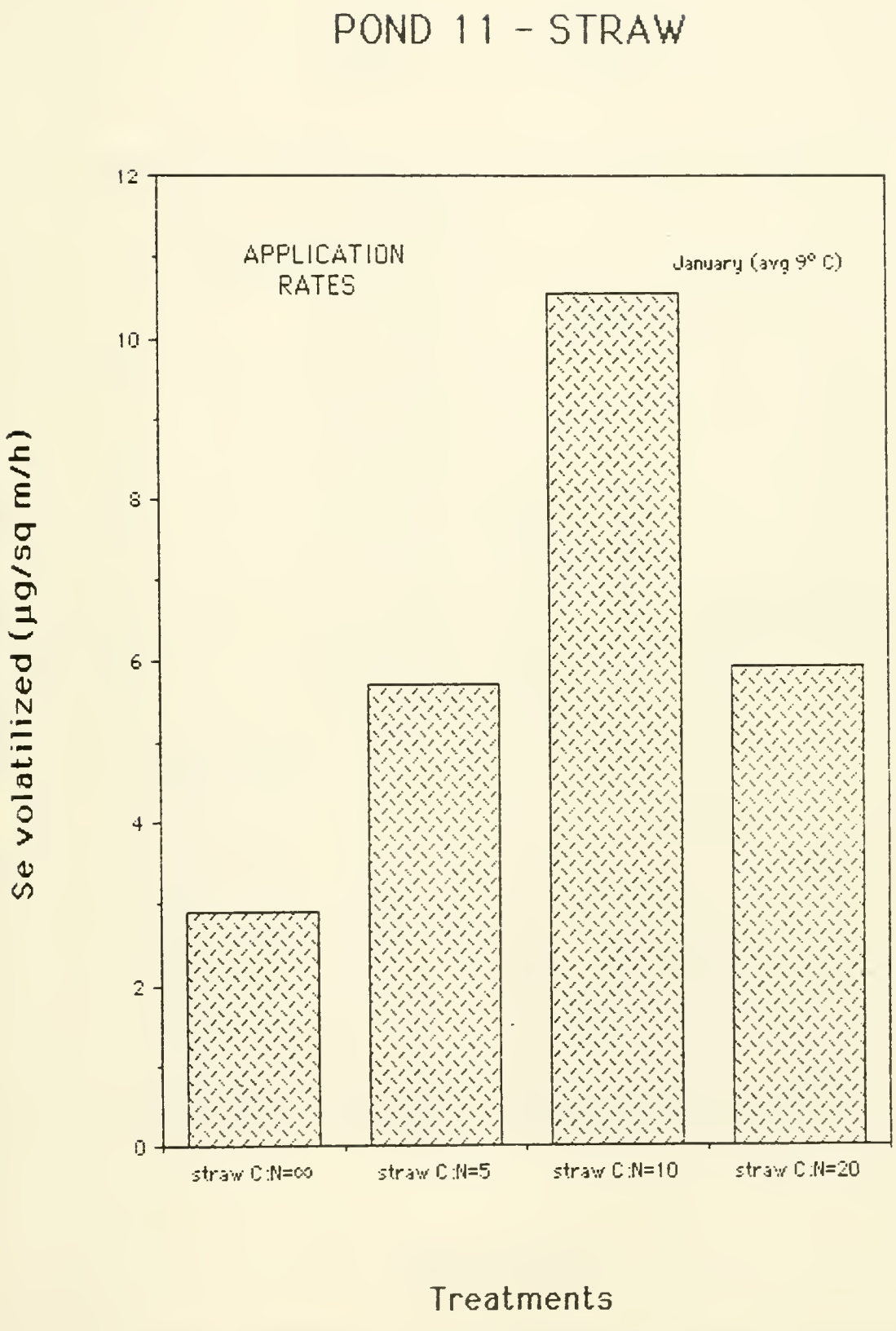


Fig. 3-9. Influence of application rates of straw on alkylselenide production in pond 11 during January 1988.

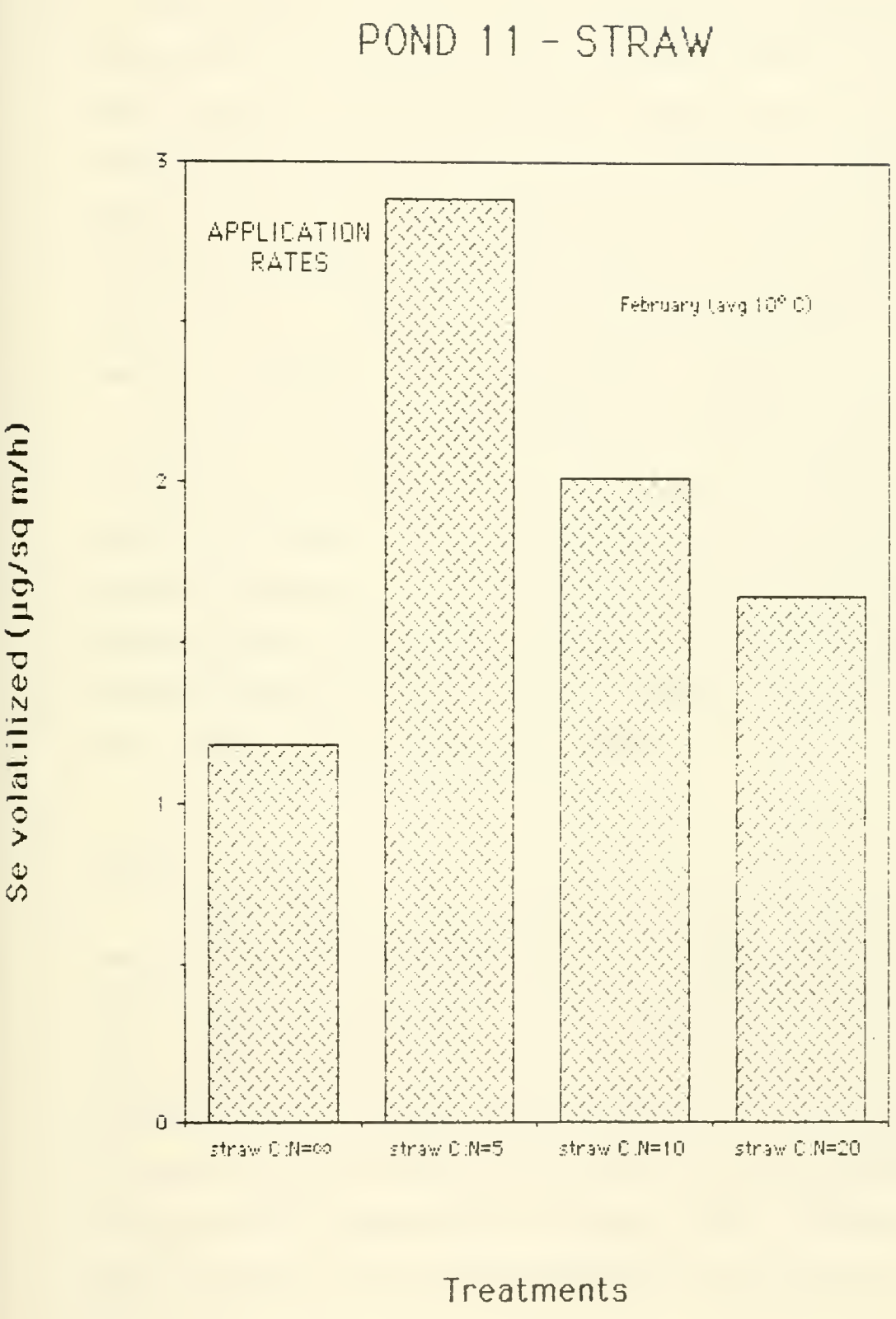


Fig. 3-10. Influence of application rates of straw on alkylselenide production in pond 11 during February 1988.

The influence of cattle manure indicates that the optimum application rate was 89 tons/acre throughout the winter months (Figs. 3-11 to 3-15). However, considerable amounts of volatile Se were observed at the lowest application rate of 41 tons/acre compared to background levels (<2 $\mu g\ m^{-2}\ h^{-1}$). The highest level of volatile Se was detected in October (average temperature, 23°C) with an average emission rate of 11.6 $\mu g\ m^{-2}\ h^{-1}$. The beneficial effect of the manure might also be a result of increasing the heat gain by solar radiation.

Among the citrus application rates, a considerable amount of volatile Se was detected at the 30 tons/acre rate in October and 14 tons/acre in November (Figs. 3-16, 3-17). During the cooler months of January and February, the higher application rates (30-45 tons/acre) promoted greater volatilization (Figs. 3-18 to 3-20). The addition of Zn and N along with citrus did little to promote alkylselenide production in pond 11 during these winter months.

Pond 4

Figures 3-21 to 3-25 illustrate the influence of treatments on the emission rates of volatile Se in pond 4. In August 1987, LBL detected the following average emission rates of volatile Se: control (47), straw (68), manure (132), and citrus (164). During the month of October, the most promising treatment appeared to be a combination of citrus and N fertilizer (plot 63) with an average emission rate of 169 $\mu g\ m^{-2}\ h^{-1}$ (October 1987 to February 1988). The highest rate of emission so far recorded from this plot was 363 $\mu g\ m^{-2}\ h^{-1}$.

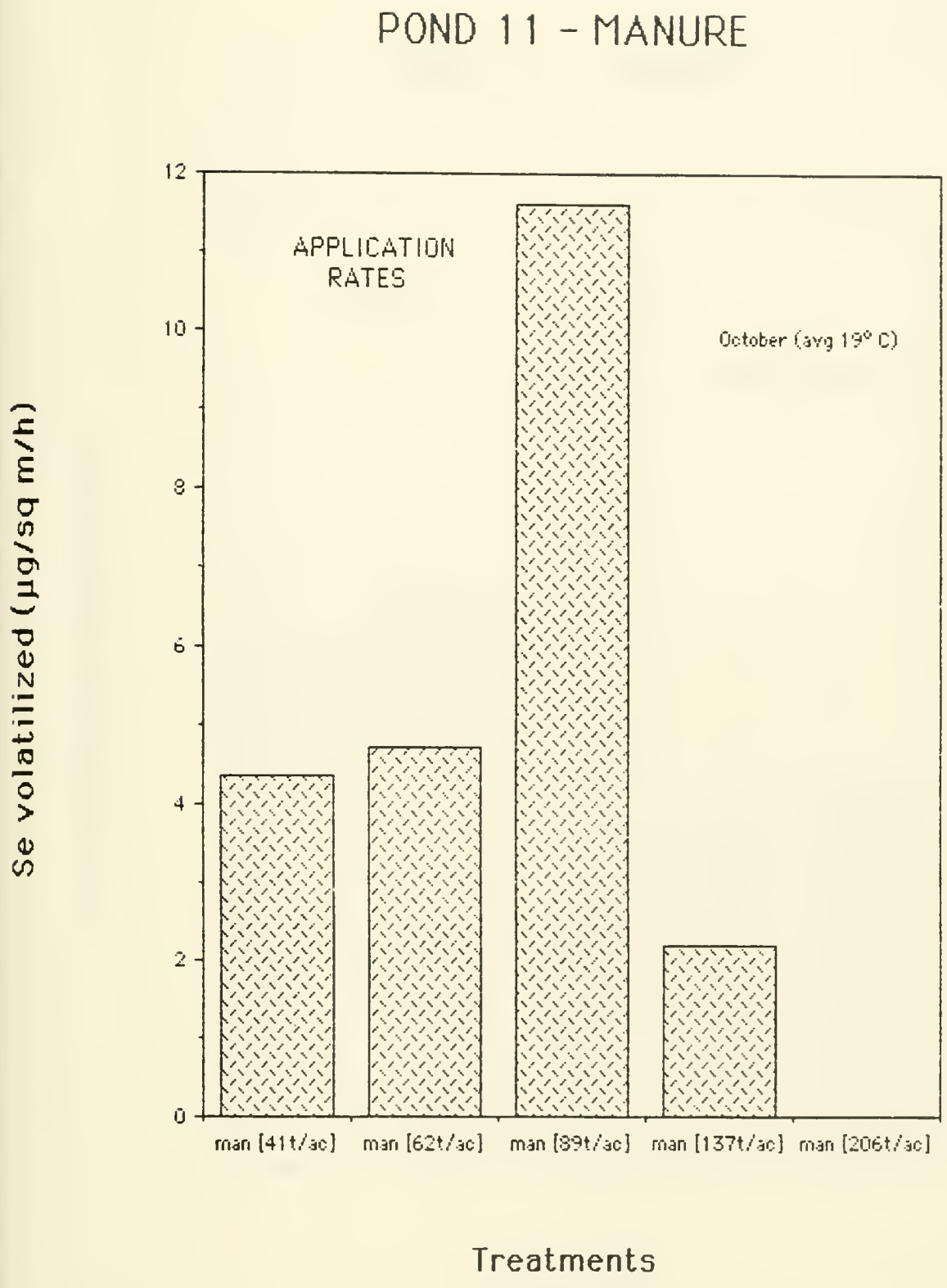


Fig. 3-11. Influence of application rates of cattle manure on alkylselenide production in pond 11 during October 1987.

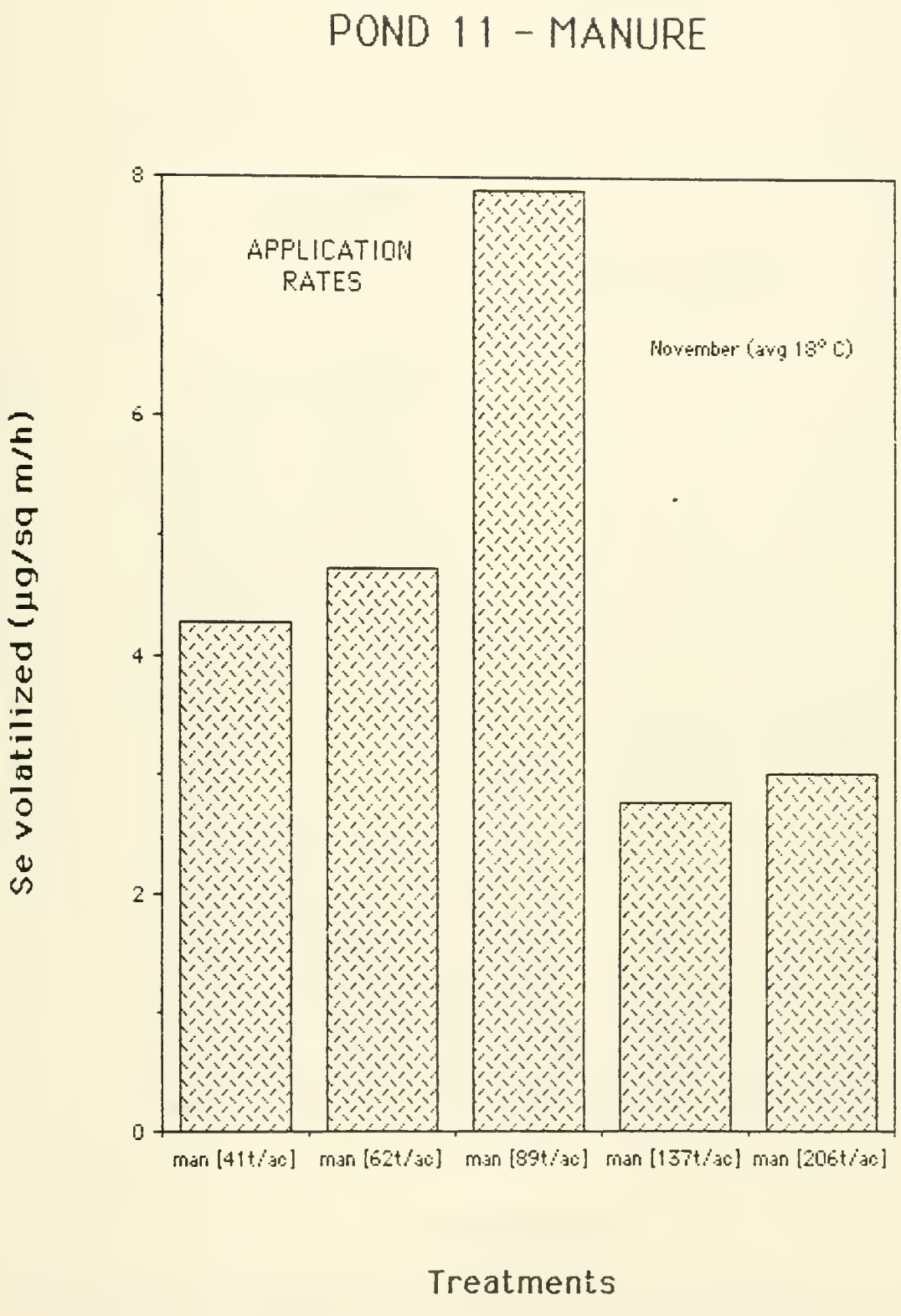


Fig. 3-12. Influence of application rates of cattle manure on alkylselenide production in pond 11 during November 1987.

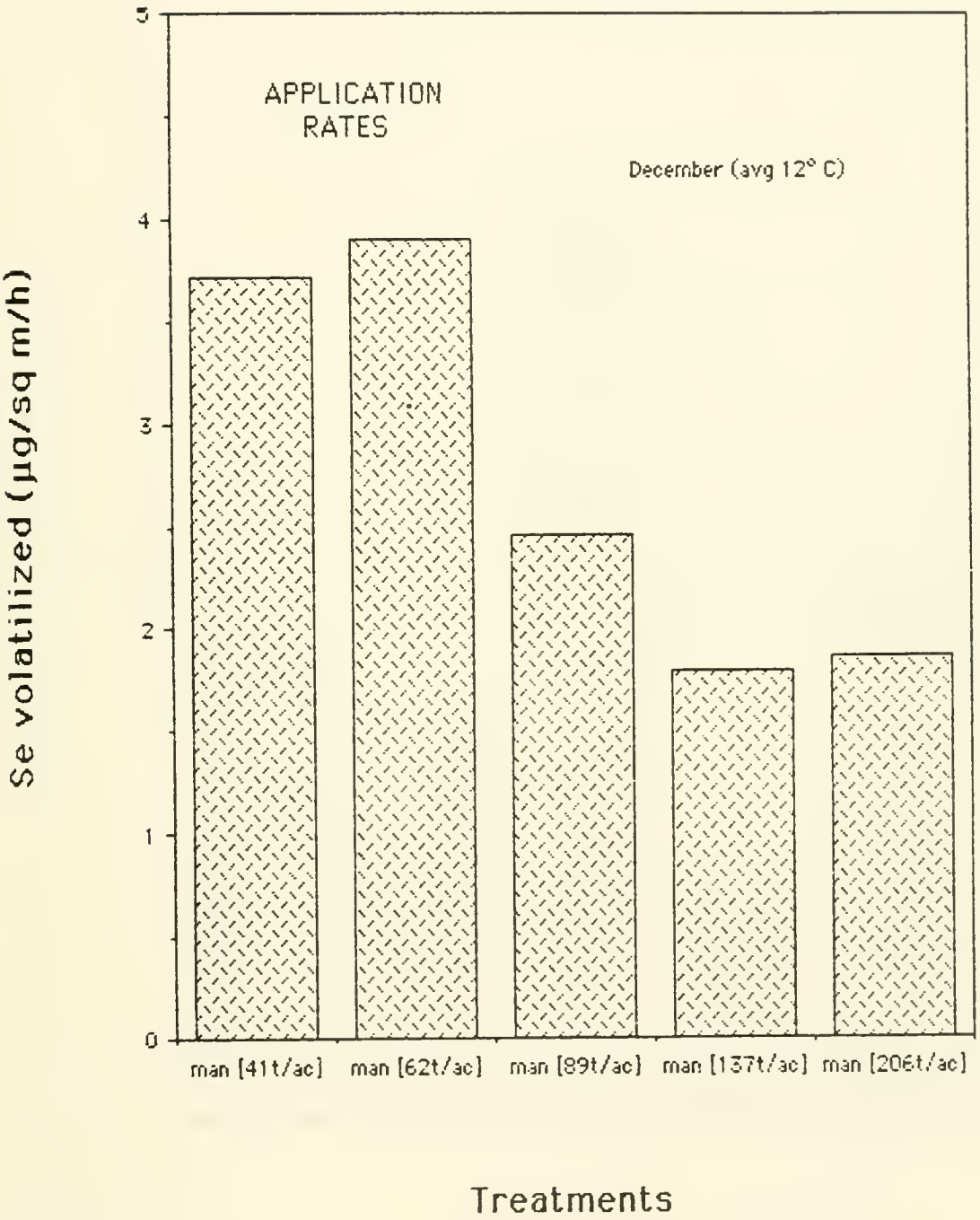


Fig. 3-13. Influence of application rates of cattle manure on alkylselenide production in pond 11 during December 1987.

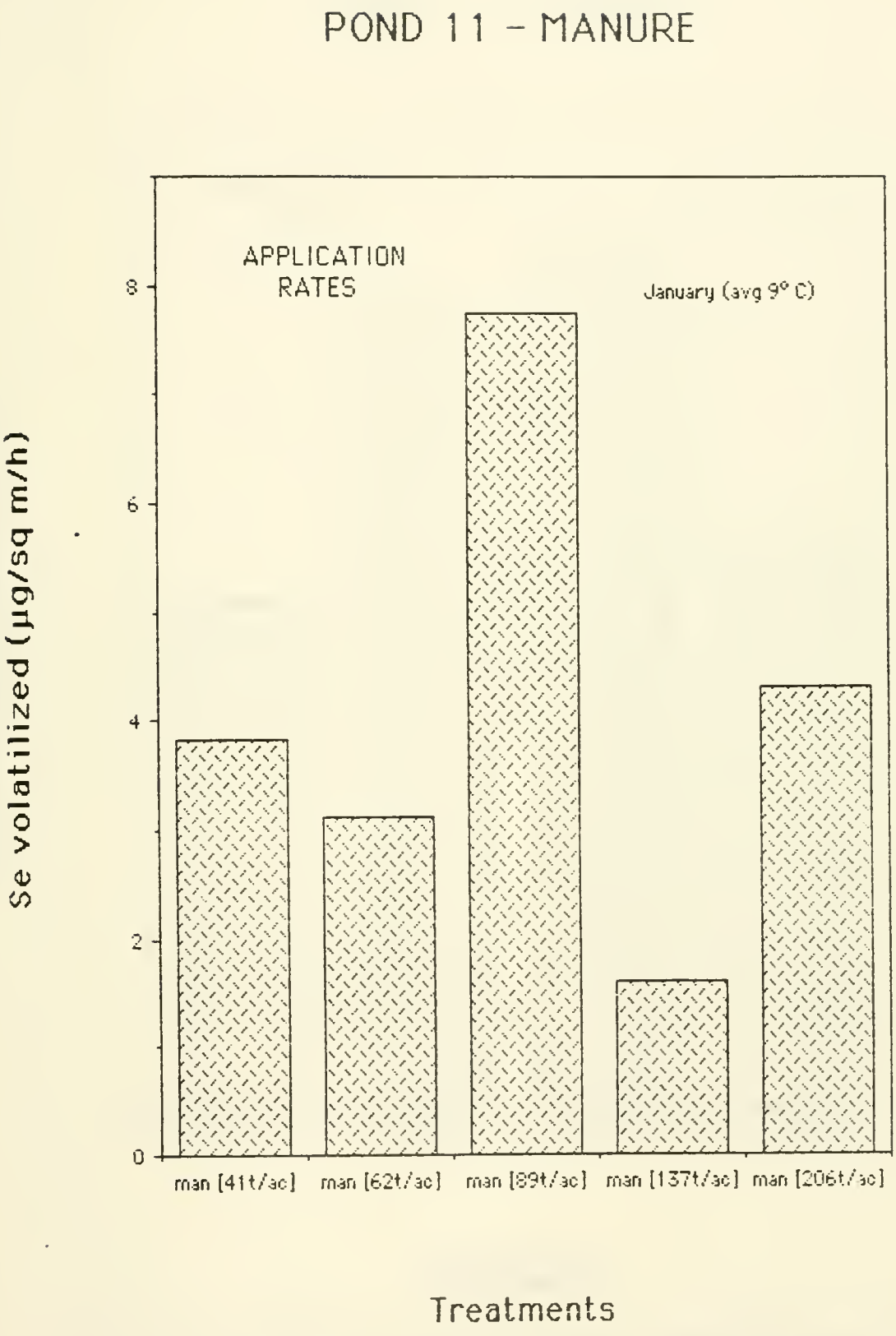


Fig. 3-14. Influence of application rates of cattle manure on alkylselenide production in pond 11 during January 1988.

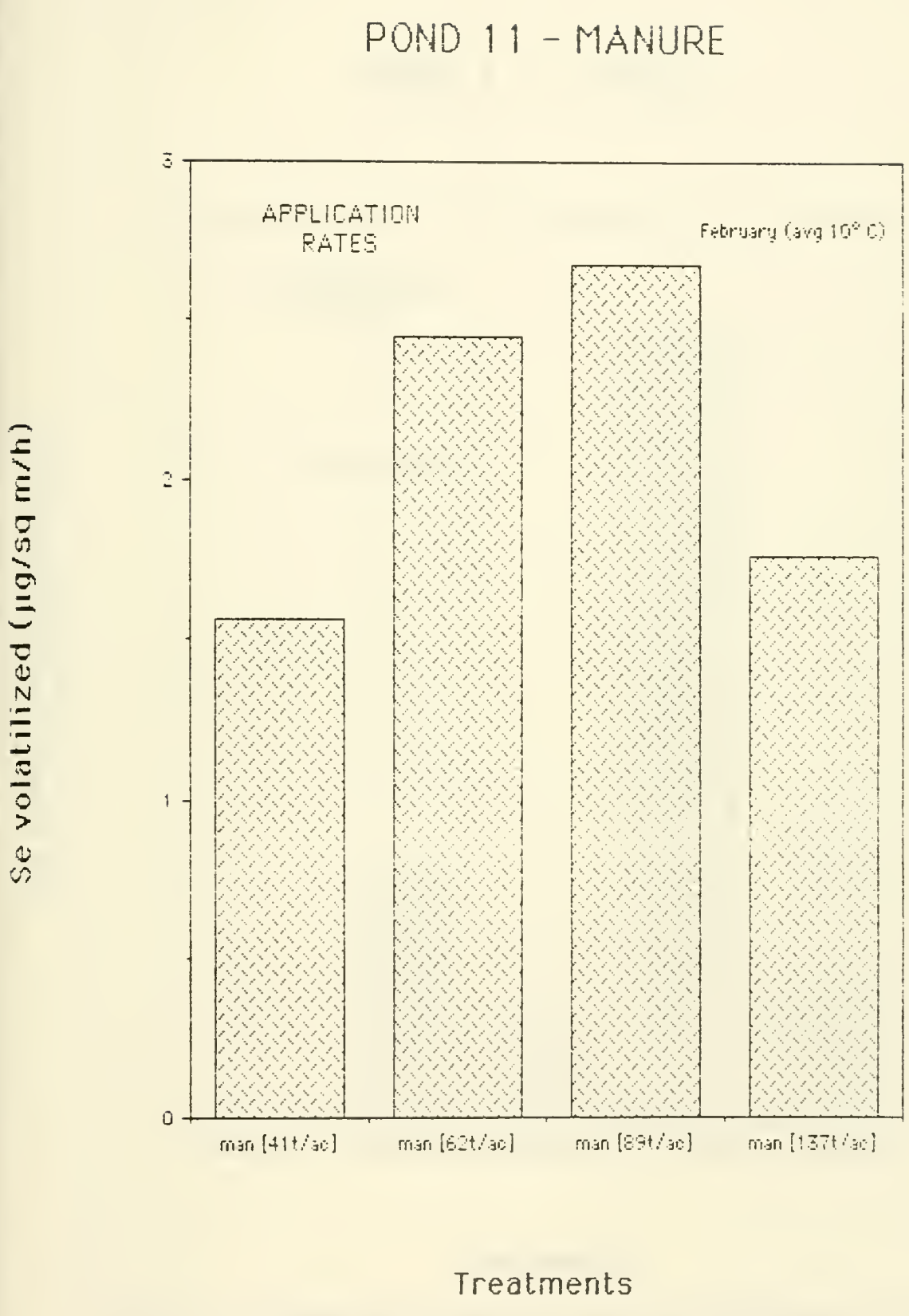


Fig. 3-15. Influence of application rates of cattle manure on alkylselenide production in pond 11 during February 1988.

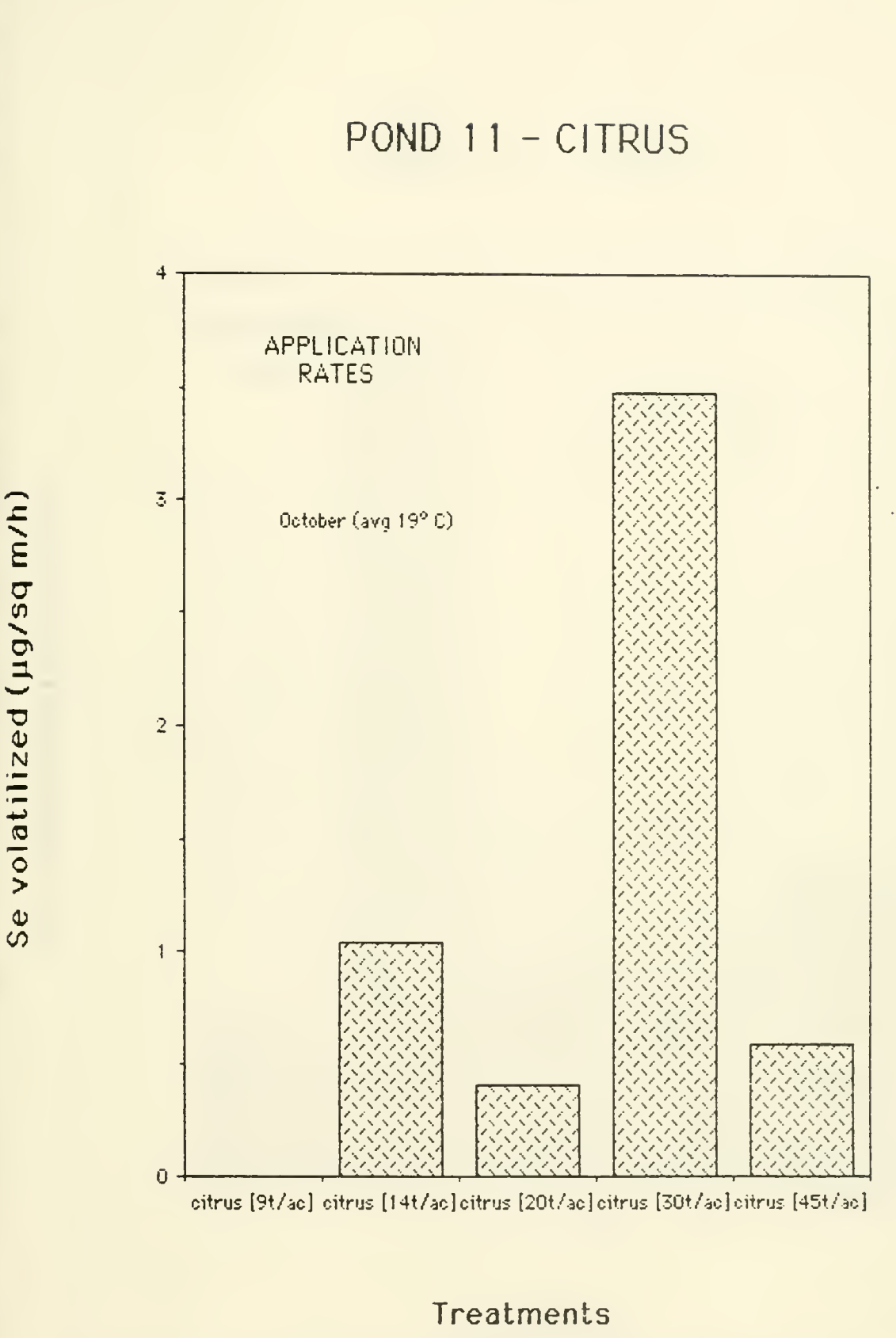


Fig. 3-16. Influence of application rates of citrus peel on alkylselenide production in pond 11 during October 1987.

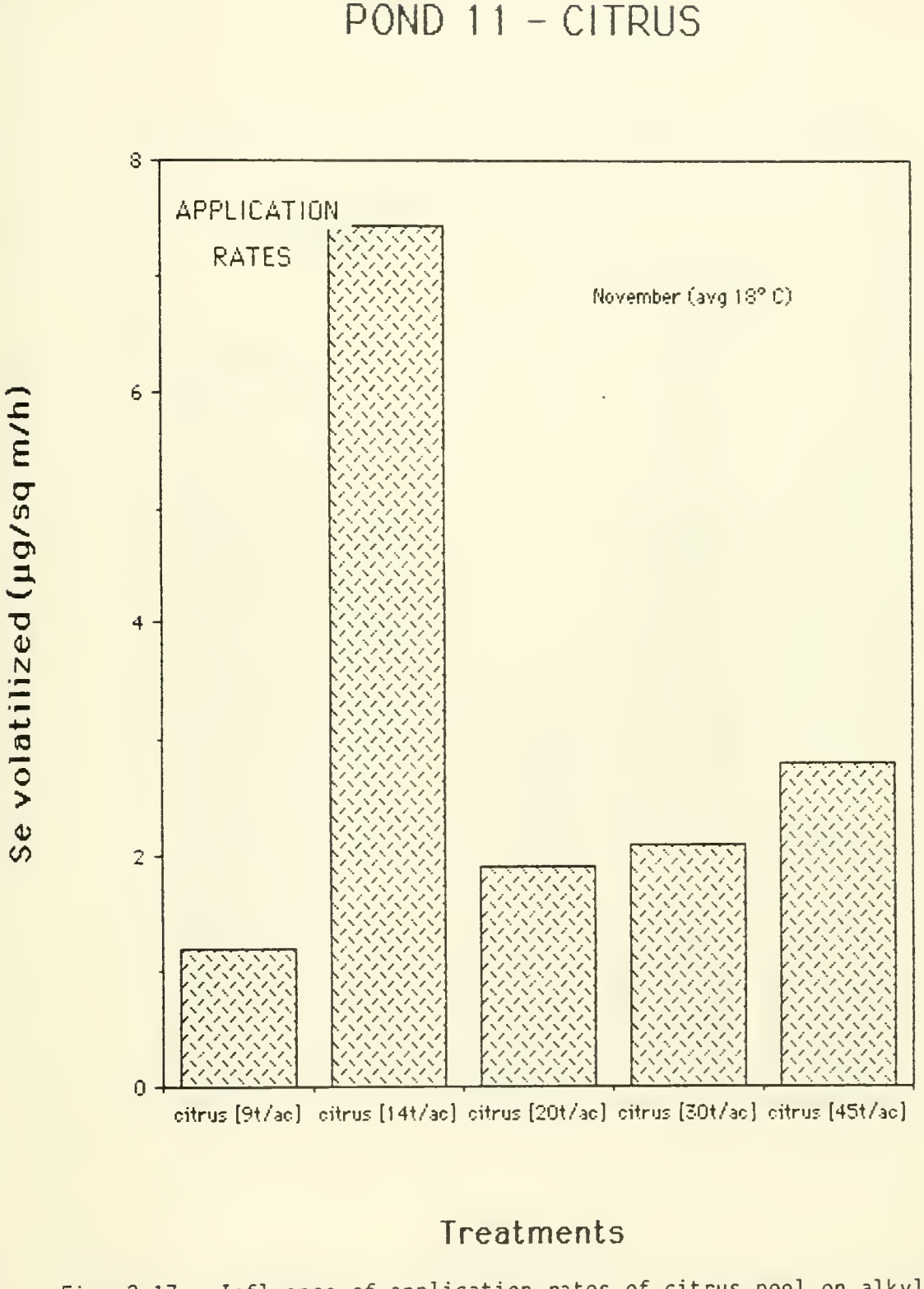


Fig. 3-17. Influence of application rates of citrus peel on alkylselenide production in pond 11 during November 1987.

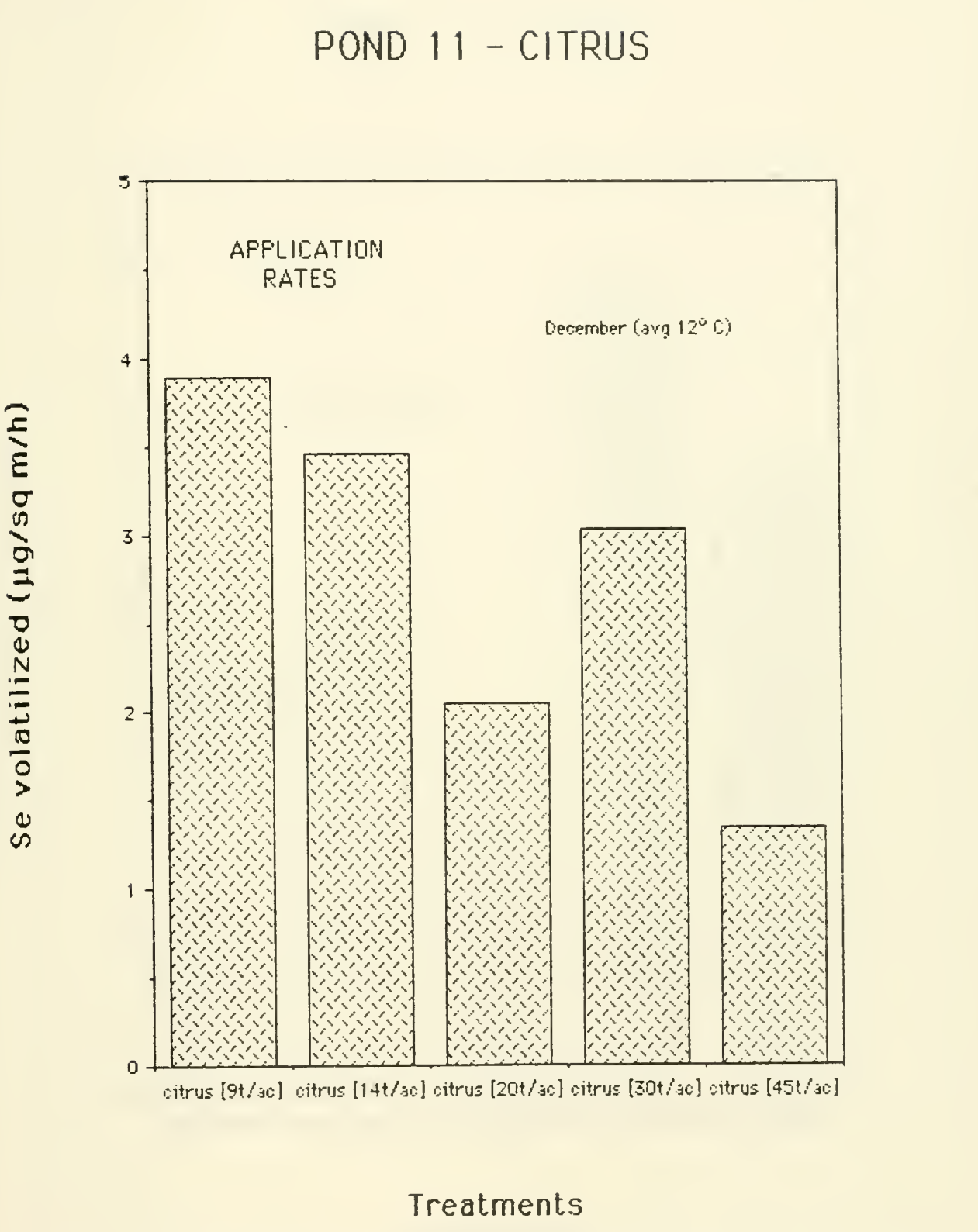


Fig. 3-18. Influence of application rates of citrus peel on alkylselenide production in pond 11 during December 1987.

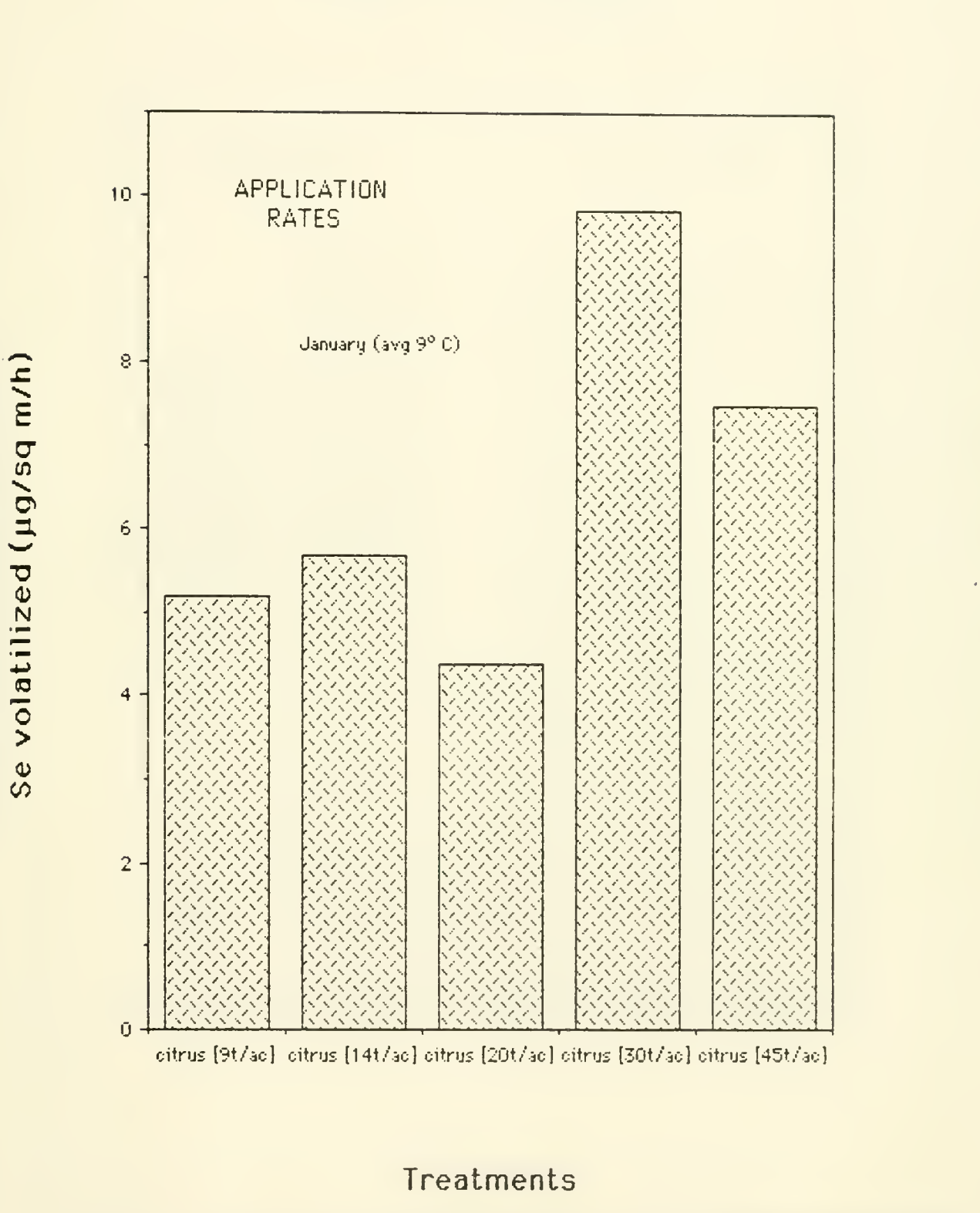


Fig. 3-19. Influence of application rates of citrus peel on alkylselenide production in pond 11 during January 1988.

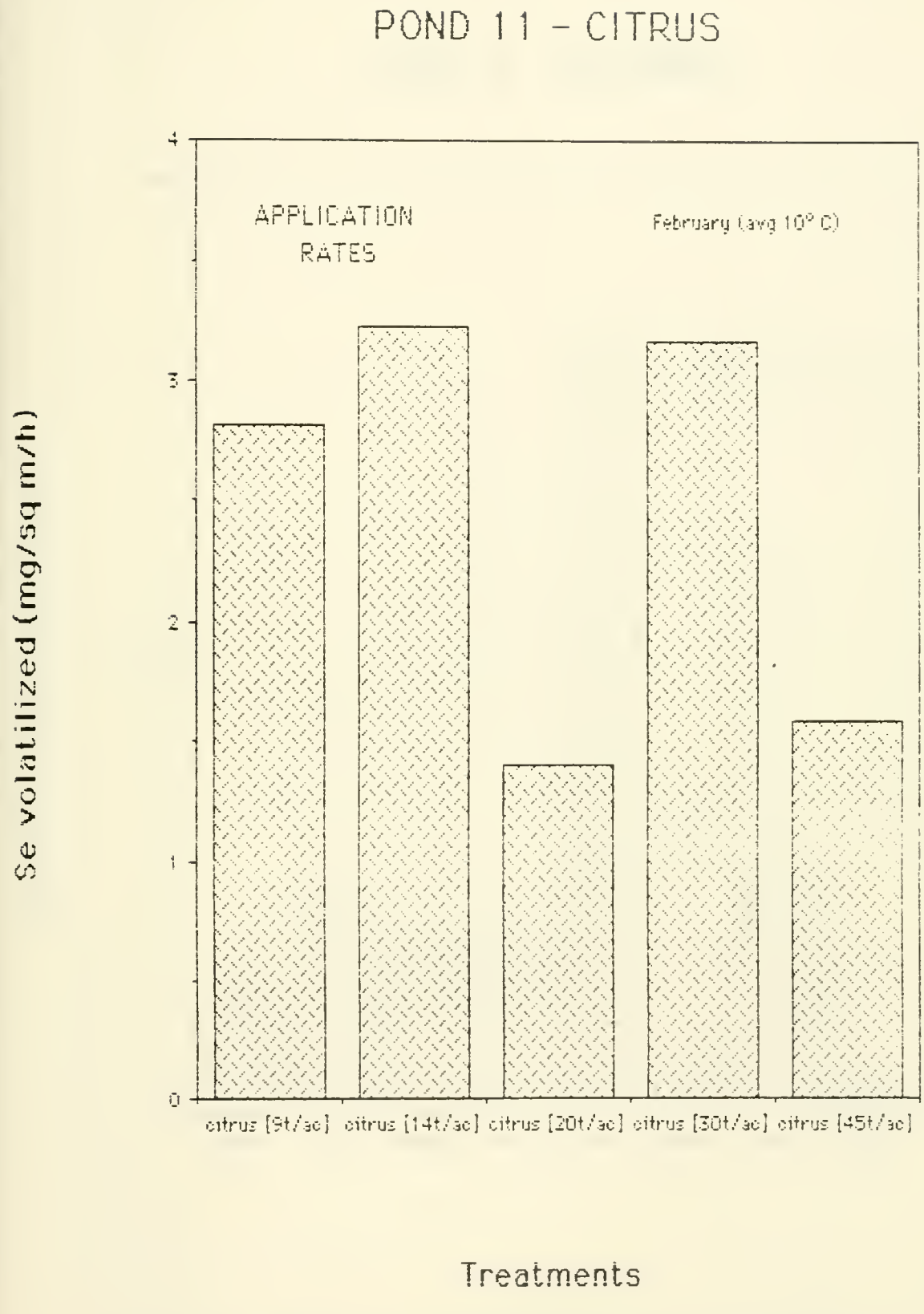


Fig. 3-20. Influence of application rates of citrus peel on alkylselenide production in pond 11 during February 1988.

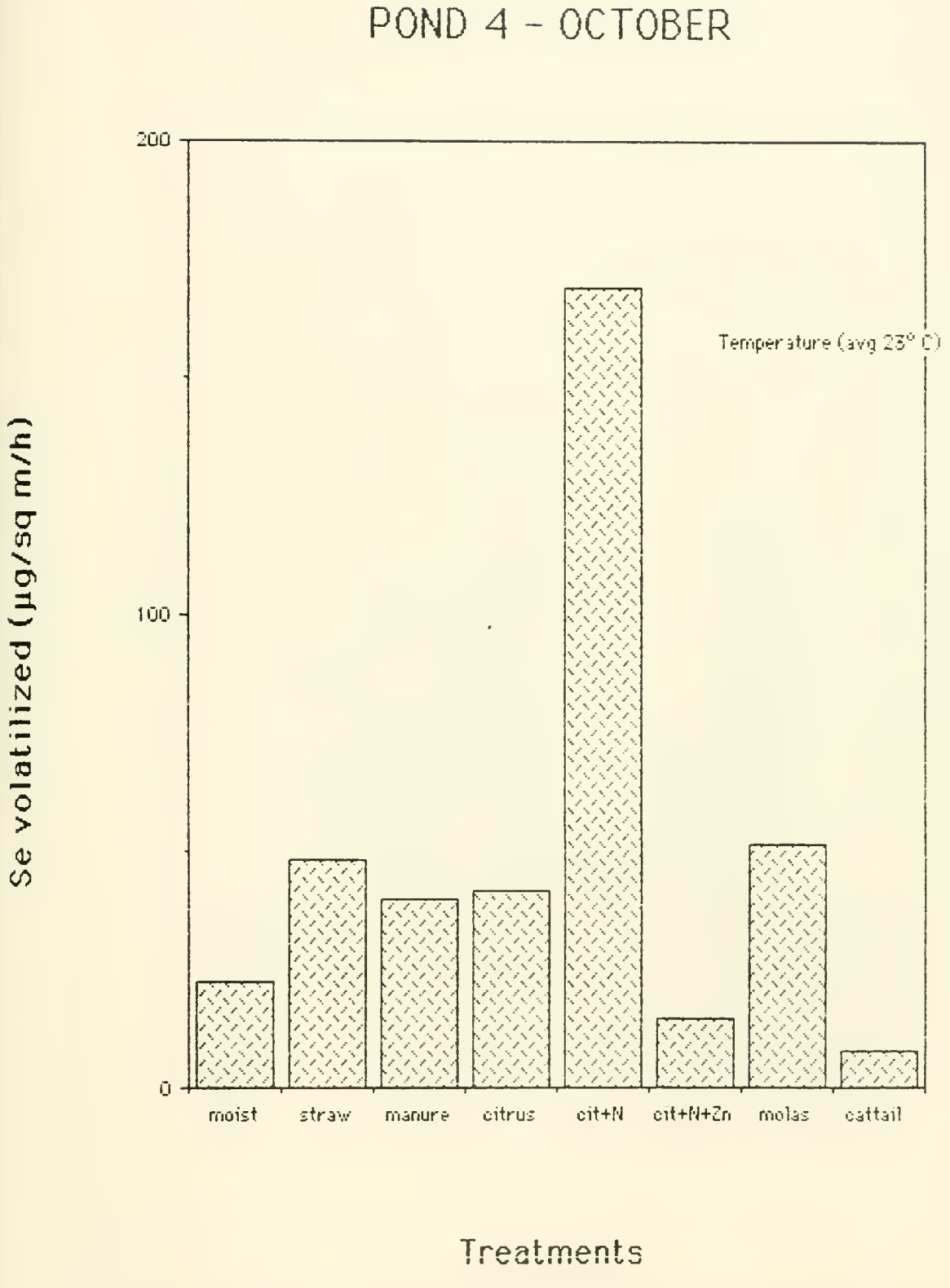


Fig. 3-21. Influence of treatments on alkylselenide production in pond 4 during October 1987.

Fig. 3-22. Influence of treatments on alkylselenide production in pond 4 during November 1987.

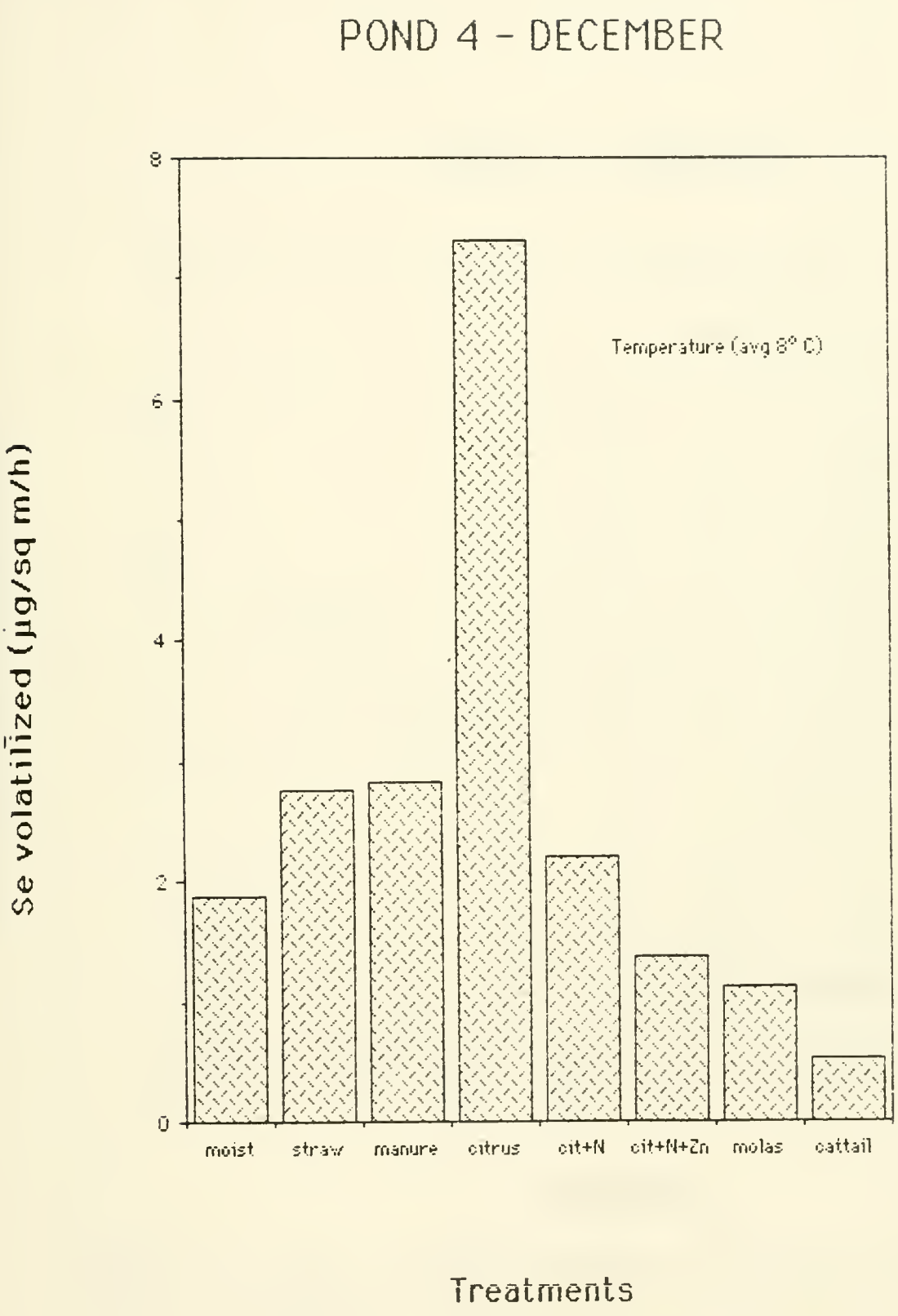


Fig. 3-23. Influence of treatments on alkylselenide production in pond 4 during December 1987.

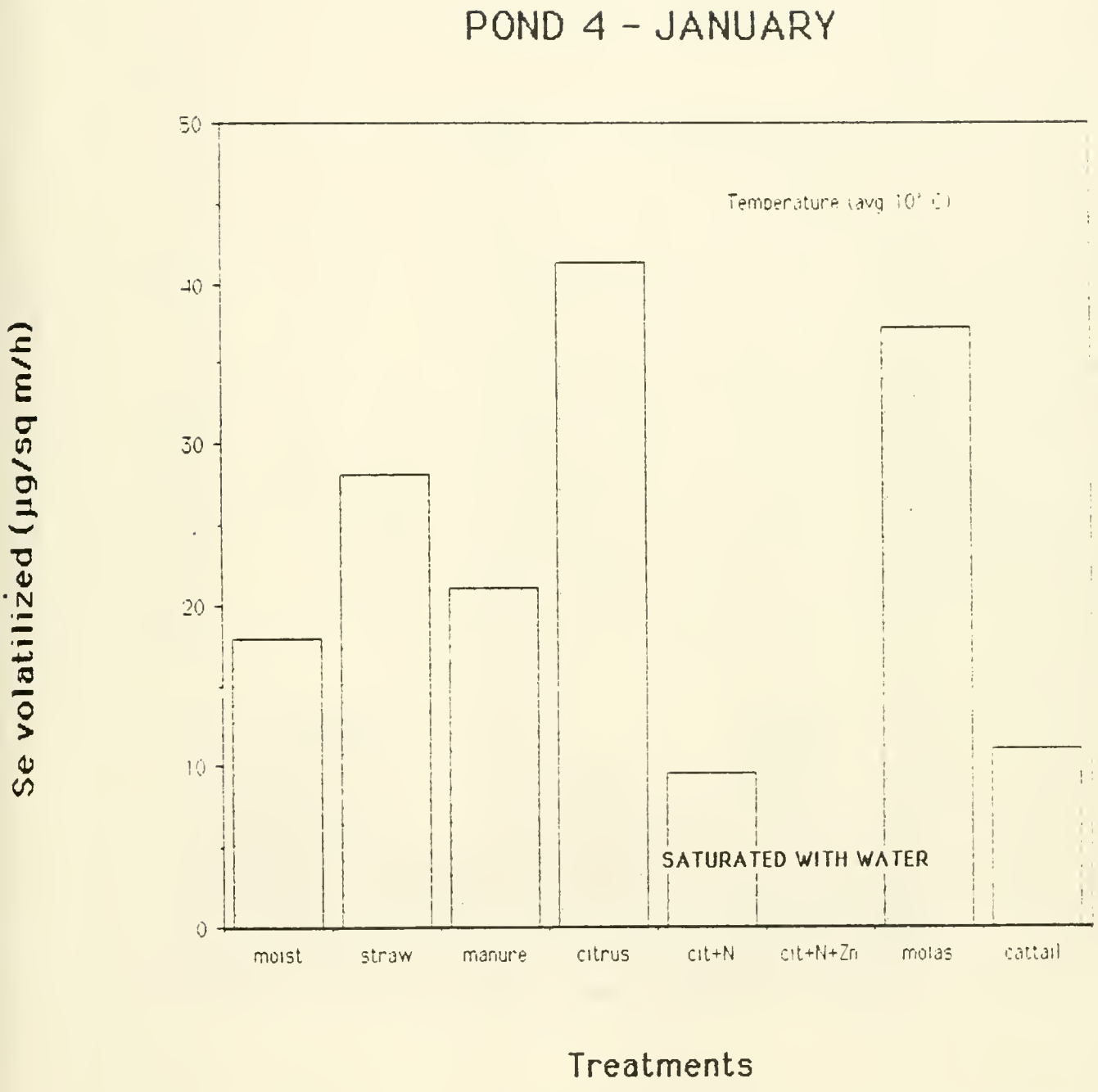


Fig. 3-24. Influence of treatments on alkylselenide production in pond 4 during January 1988.

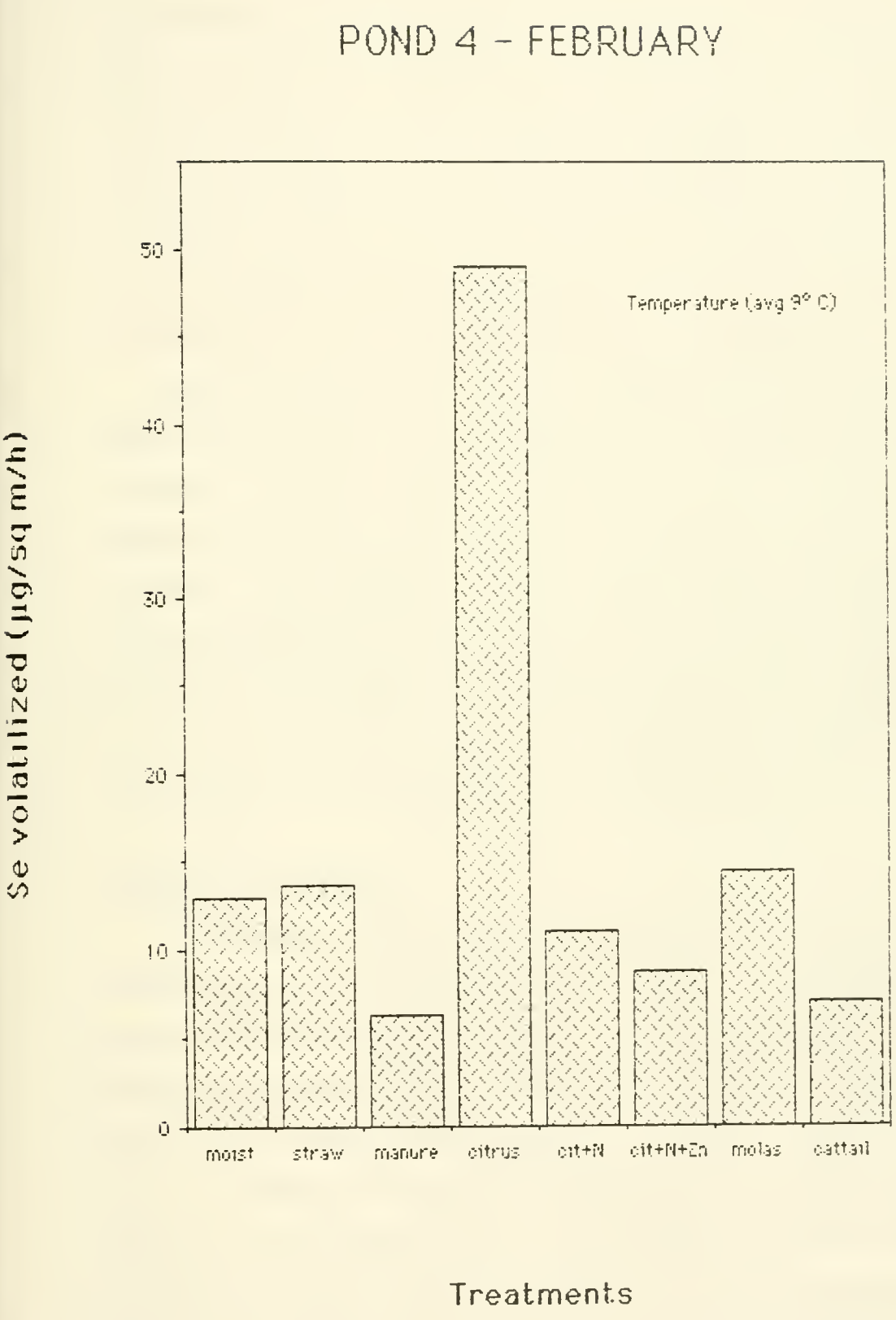


Fig. 3-25. Influence of treatments on alkylselenide production in pond 4 during February 1988.

This particular treatment promoted the biomethylation reaction 22.3-fold greater than the moist treatment alone and 59-fold more than background Se emission (2.86 $\mu g\ m^{-2}\ h^{-1}$). However, this subplot soon became saturated with water as well as many other subplots on the east end of our experimental plots. This was a result of a rising water table. As the soils became waterlogged, the emission rates of Se diminished. This is particularly evident with the citrus + N + Zn treatment in January 1988.

Overall, the citrus and molasses treatments were the best to enhance biomethylation of Se throughout the winter months (particularly in November, December, January, and February). The citrus treatment enhanced alkylselenide production over the moist treatment by 3.57X (November), 2.27X (December), 2.45X (January), and 11.3X (February). The cattle manure and straw treatments were less effective than citrus, but moreso than irrigation alone. The average background emission rates ($\mu g\ m^{-2}\ h^{-1}$) of Se were as follows: 2.86 (October), 3.44 (November), 1.04 (December), 3.02 (January), and 1.59 (February).

Influence of Temperature

A laboratory study was conducted to determine the influence of temperature on the biomethylation of Se in soil. Soil obtained from pond 4 at Kesterson was added (25 g) to a 125-mL Erlenmeyer flask and moistened with deionized water to approximately 70% WHC, capped with a Mininert valve (Teflon) and incubated up to 8 days. At 24 h intervals, a 1-mL gas sample was taken from the headspace and injected into a Shimadzu gas chromatograph with a flame ionization detector (FID). The dimethylselenide produced was compared to reference standards and results were reported in ppb. Figure 3-26 indicates that the rate of Se

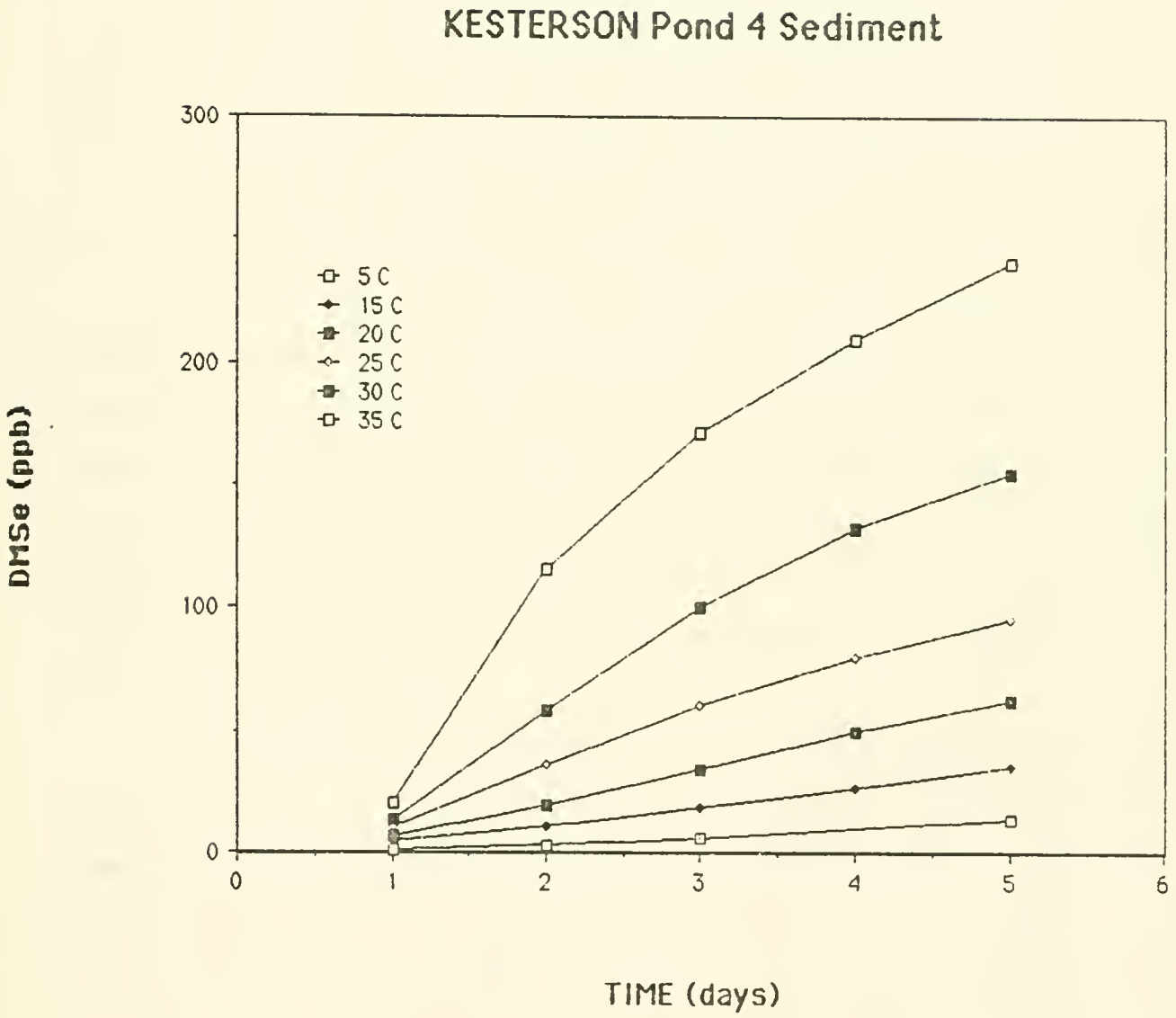


Fig. 3-26. Influence of temperature on alkylselenide production of Se in soil.

methylation increased with increasing temperature (5-35°C). One set of soils was treated with D-galacturonic acid (2 mg C g^{-1} soil) and incubated at 25°C. With the addition of C, the rate of the biomethylation reaction was increased 2.63-fold over that without added C and incubated at the same temperature (Fig. 3-27). In terms of thermodynamics, the average Q_{10} was calculated to be 2.60 and the activation energy = 67.4 kJ mol^{-1} (Fig. 3-28). That is, for every 10°C rise in temperature, the rate of biomethylation of Se without added C was increased 2.60-fold. Adding C was as effective in promoting biomethylation of Se as raising the temperature 10°C.

The diurnal activity of volatile Se production in the field was monitored in October, 1987 (Fig. 3-29). Results indicate that the peak of activity is during mid-afternoon. The volatile Se emission rate from plot 63 (citrus, N, Zn) was the highest ever recorded during 1-2 pm (363 $\mu g\ m^{-2}\ h^{-1}$). A simple linear regression analysis of the data collected from October through December 1987 of plot 63 indicated that the volatile Se flux was highly dependent upon atmospheric temperature (r^2 = 0.724**) (Fig. 3-30).

During the month of February 1988, volatile Se was monitored in 3 plots (57, moist; 58, 61 citrus) along with the atmospheric and soil temperatures (Figs. 3-31 to 3-35). Diurnal cycling of volatile Se was evident showing a peak of Se emission during mid- to late day. Among the 3 plots, the peak of volatile Se flux was from 2-4 pm, lagging just behind the peak of atmospheric and soil temperature readings. A linear

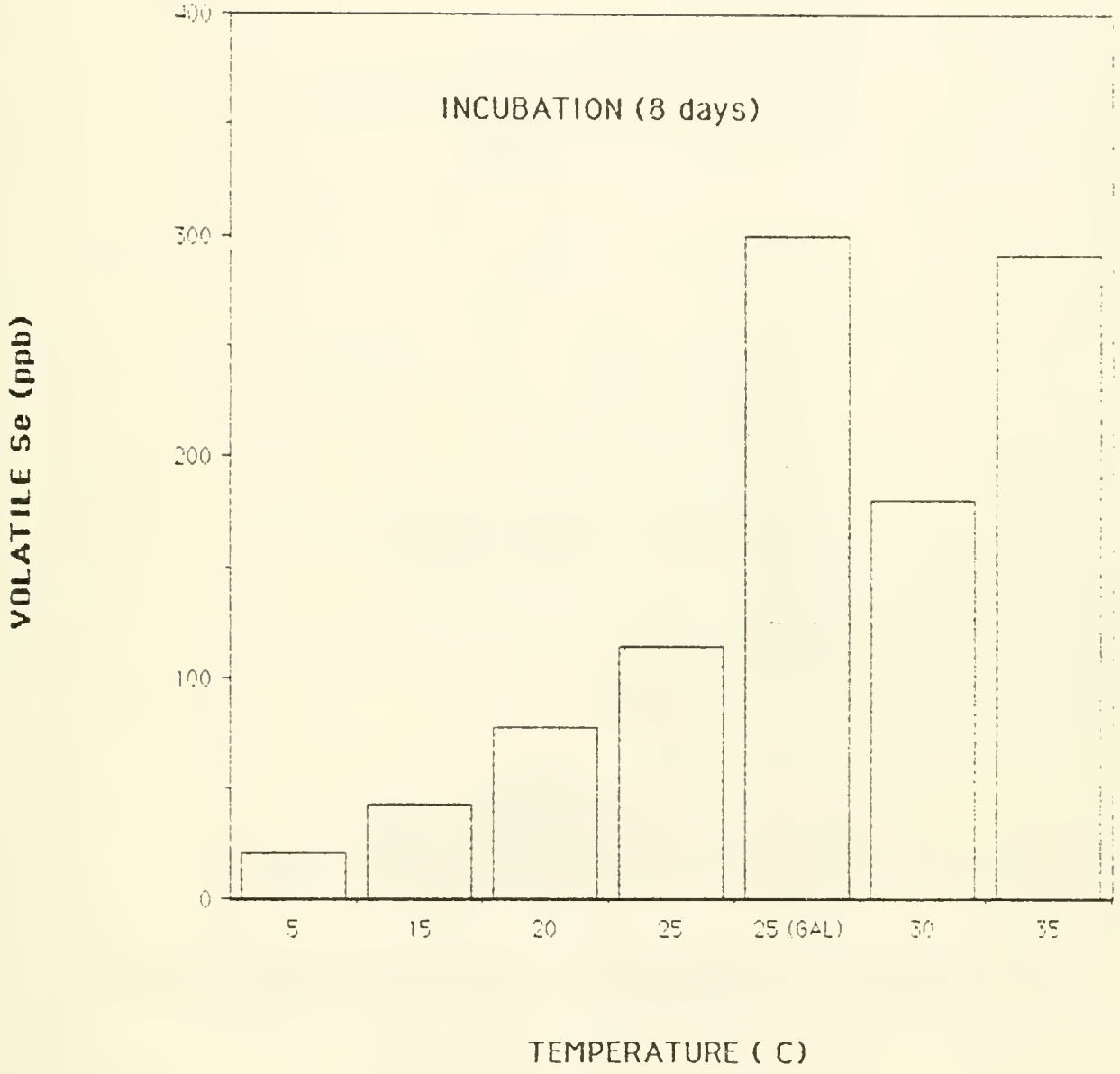
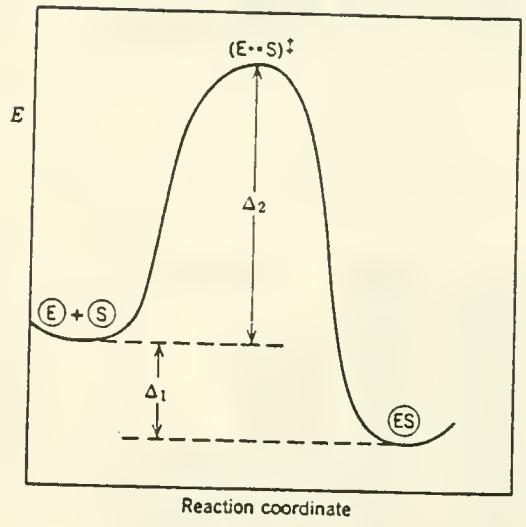


Fig. 3-27. Influence of temperature on alkylselenide production in soil (Kesterson, pond 4) after 8 days of incubation. GAL represents D-galacturonic acid (2 mg C g^{-1} soil).

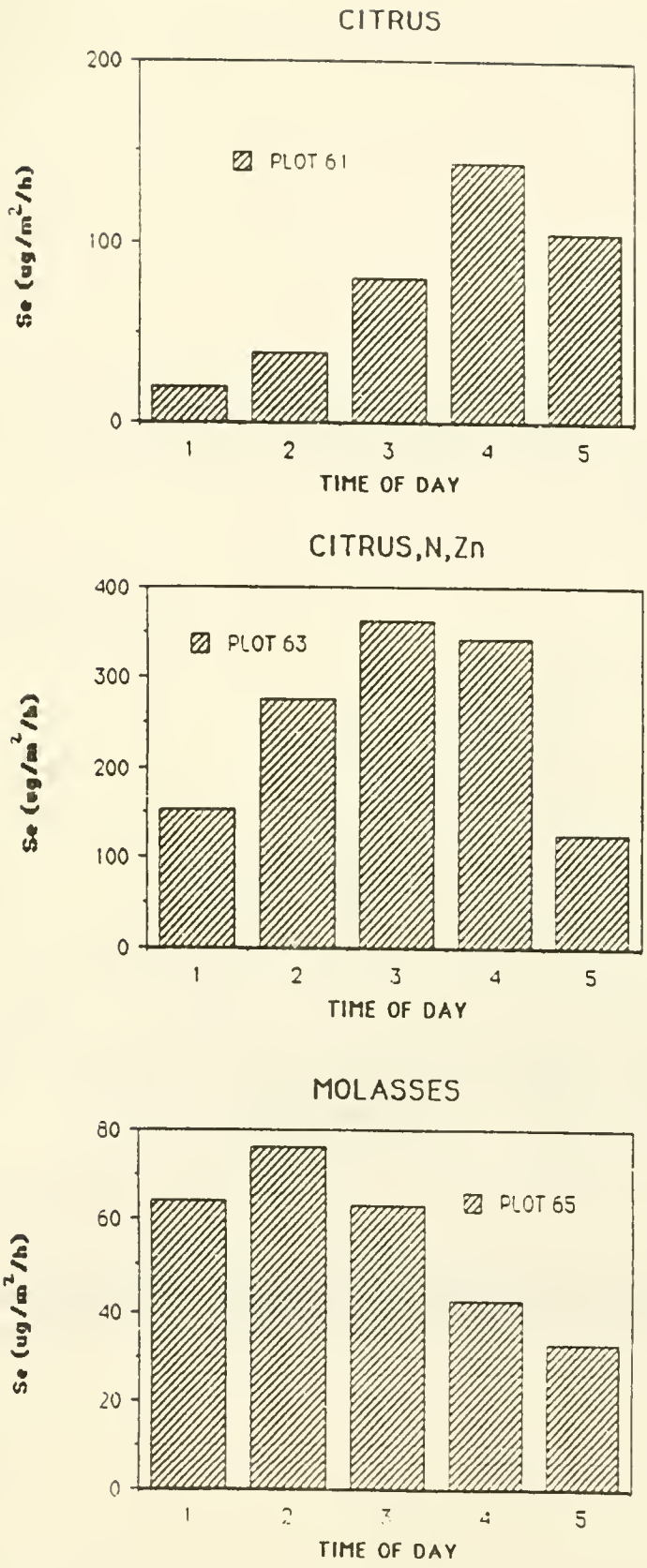


E_a Biomethylation of Se = 67.4 kJ mol^{-1} .

Avg Q_{10}^{*} = 2.60

$$^{*}Q_{10} = \frac{10{,}000\ E_a}{RT\ (T + 10)}$$

Fig. 3-28. Thermodynamics of the biomethylation of Se in soil.



TIME OF DAY:

1	9-10 a.m.
2	11-12 a.m.
3	1-2 p.m.
4	3-4 p.m.
5	5-6 p.m.

Fig. 3-29. Diurnal measurements of alkylselenide production in October 1987.

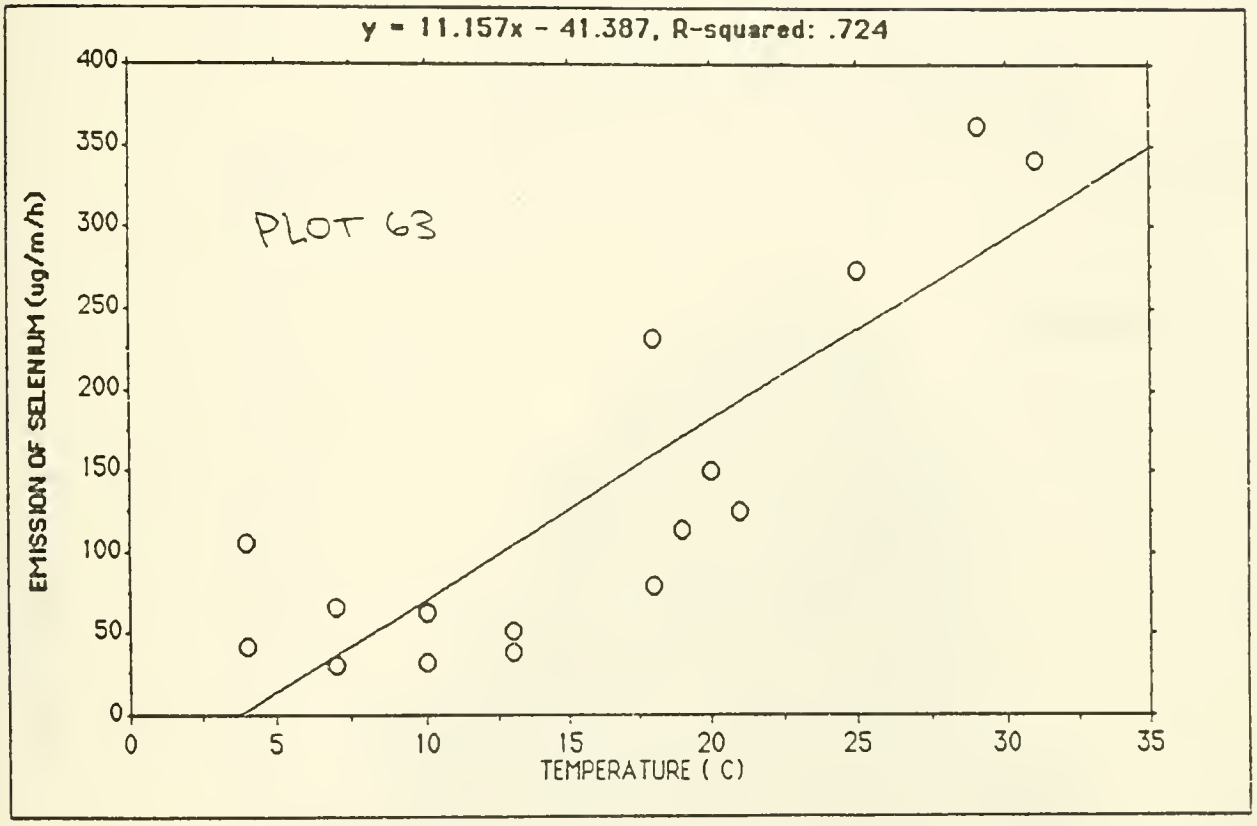


Fig. 3-30. Linear regression analysis of alkylselenide production in plot 63 and atmospheric temperature from October-December 1987.

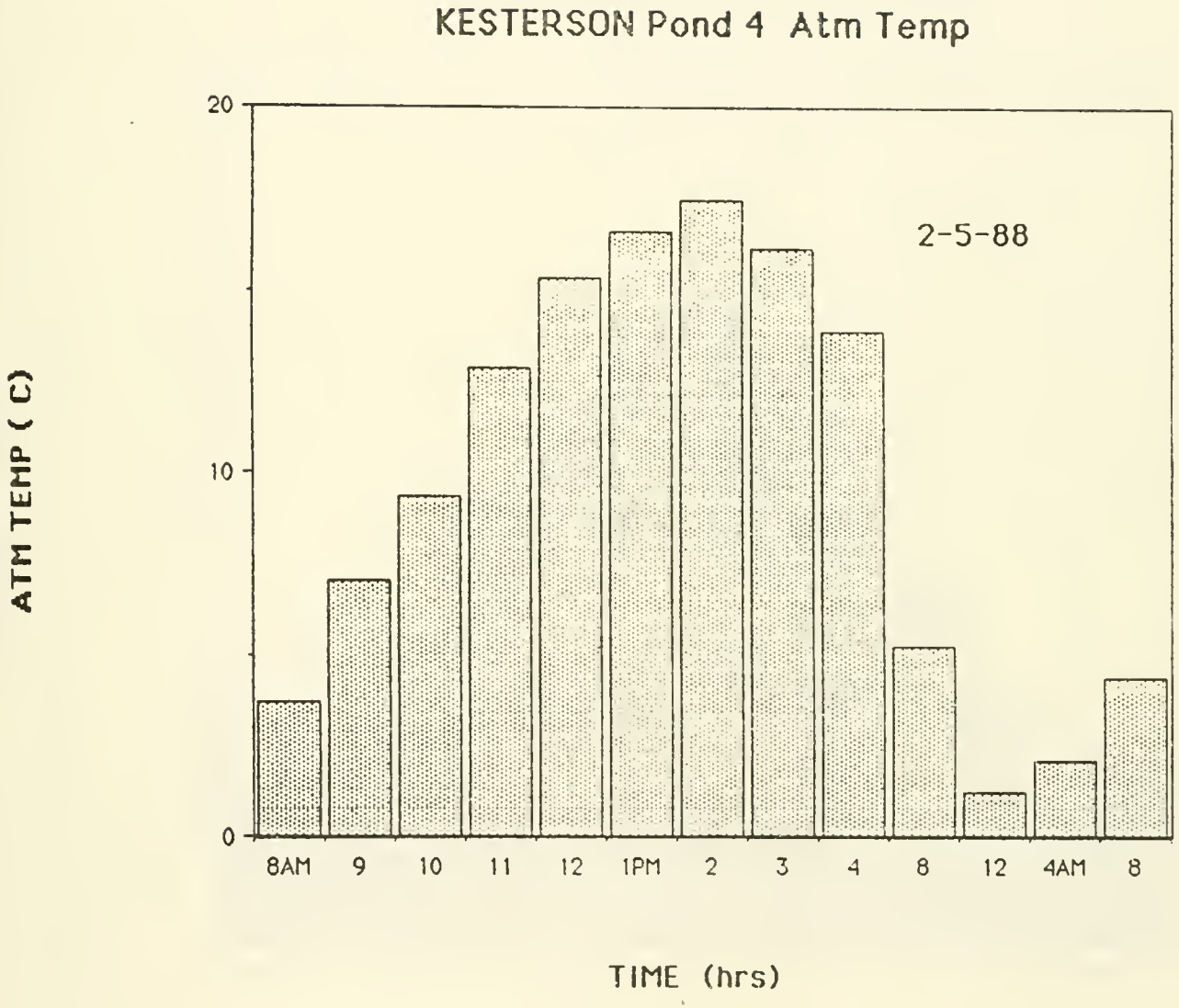


Fig. 3-31. Diurnal measurements of atmospheric temperature in February 1988.

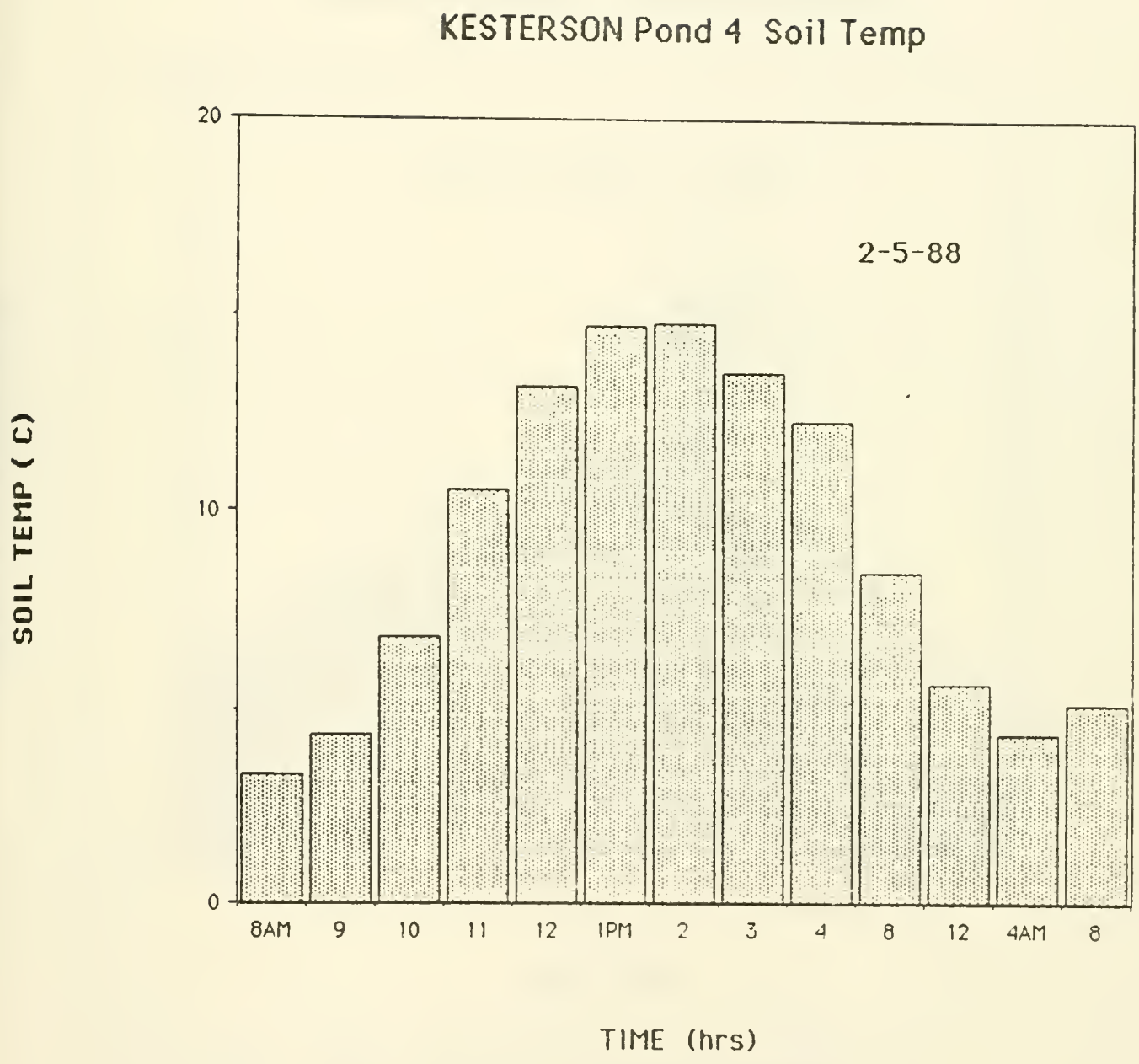


Fig. 3-32. Diurnal measurements of soil temperature in February 1988.

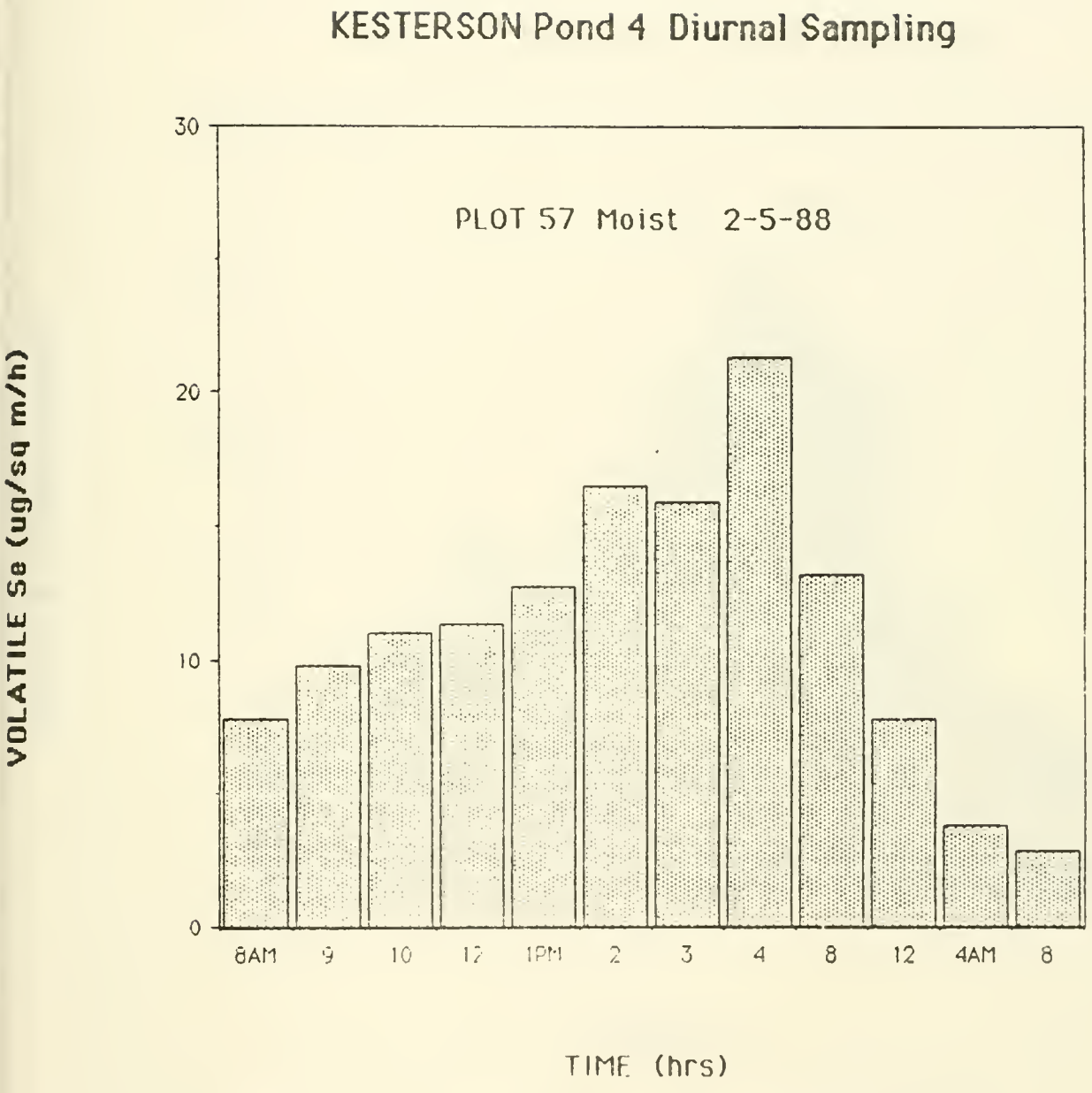


Fig. 3-33. Diurnal measurements of volatile selenium from pond 57 in February 1988.

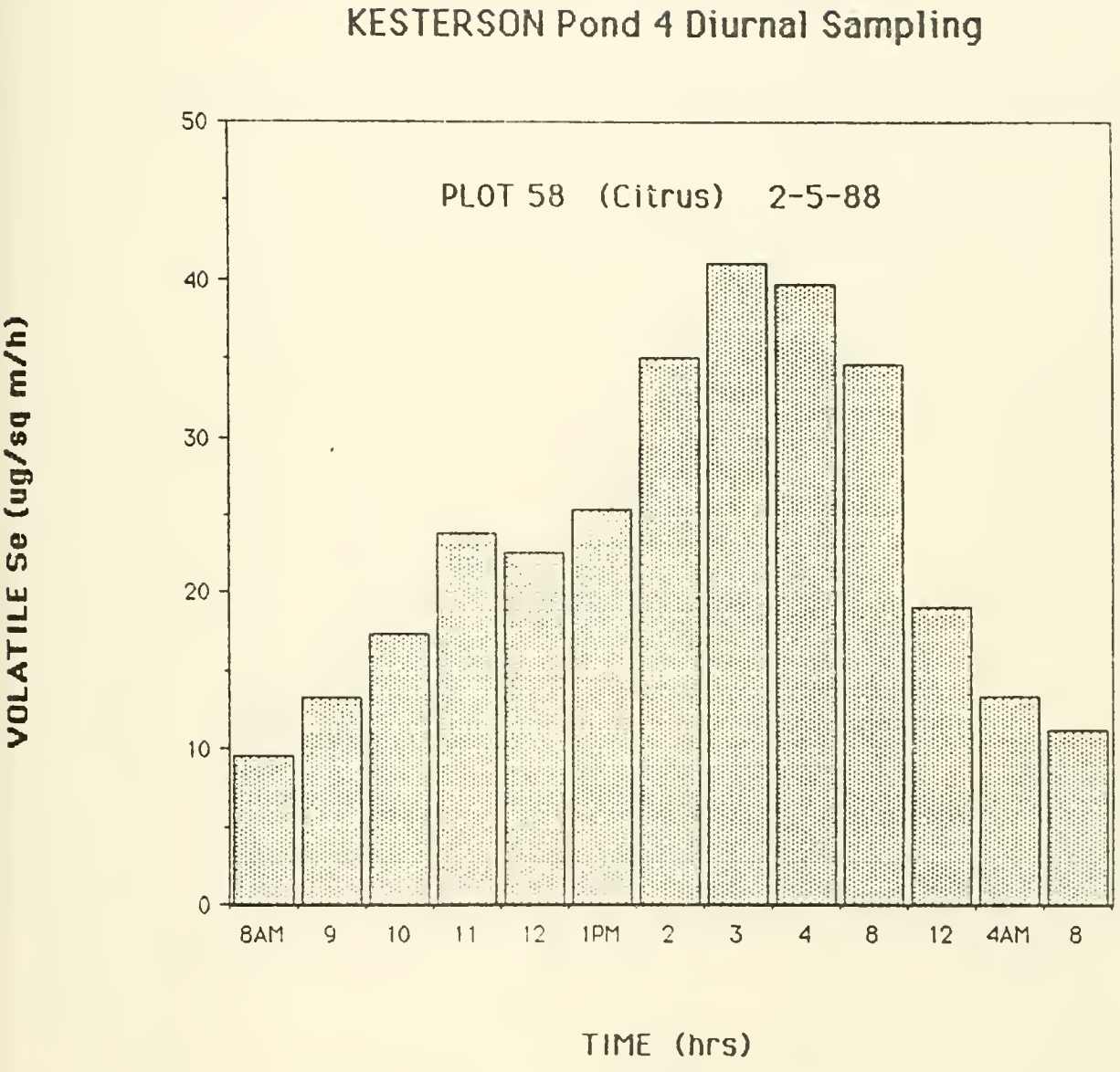


Fig. 3-34. Diurnal measurements of volatile selenium from pond 58 in February 1988.

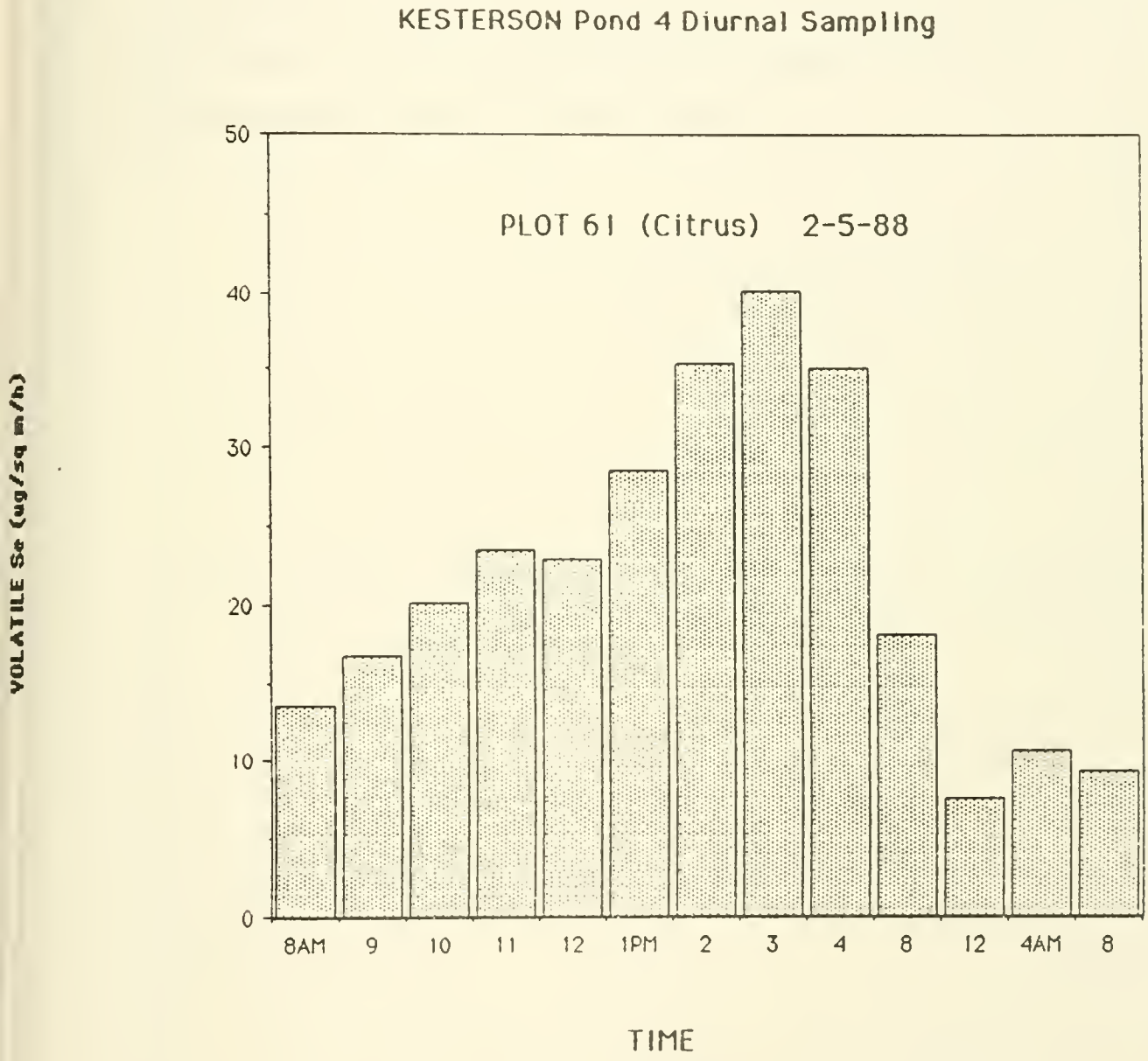
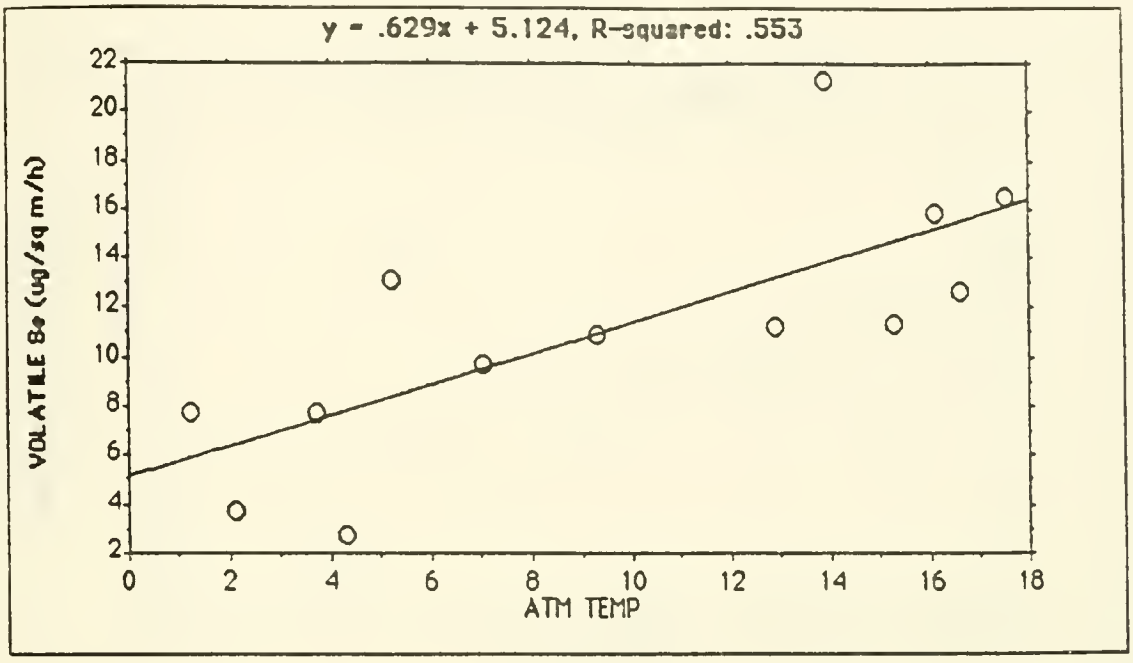


Fig. 3-35. Diurnal measurements of volatile selenium from pond 61 in February 1988.

regression analysis was made between the volatile Se flux of all 3 plots and atmospheric and soil temperature. In most cases, the correlation coefficient for estimating the biomethylation rates based upon temperature was highly significant at the 5% level (Figs. 3-36 to 3-38).

The diurnal cycling and the temperature coefficient data indicate that Se emission rates will be dramatically increased during the spring and summer months with warmer temperatures.

PLOT 57



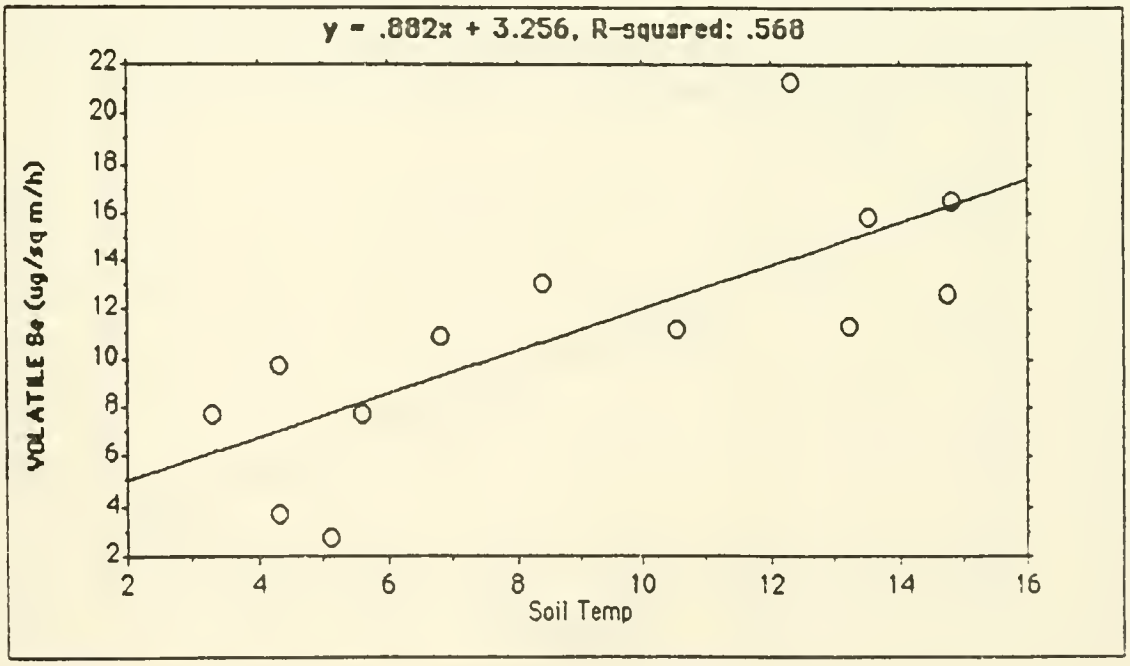
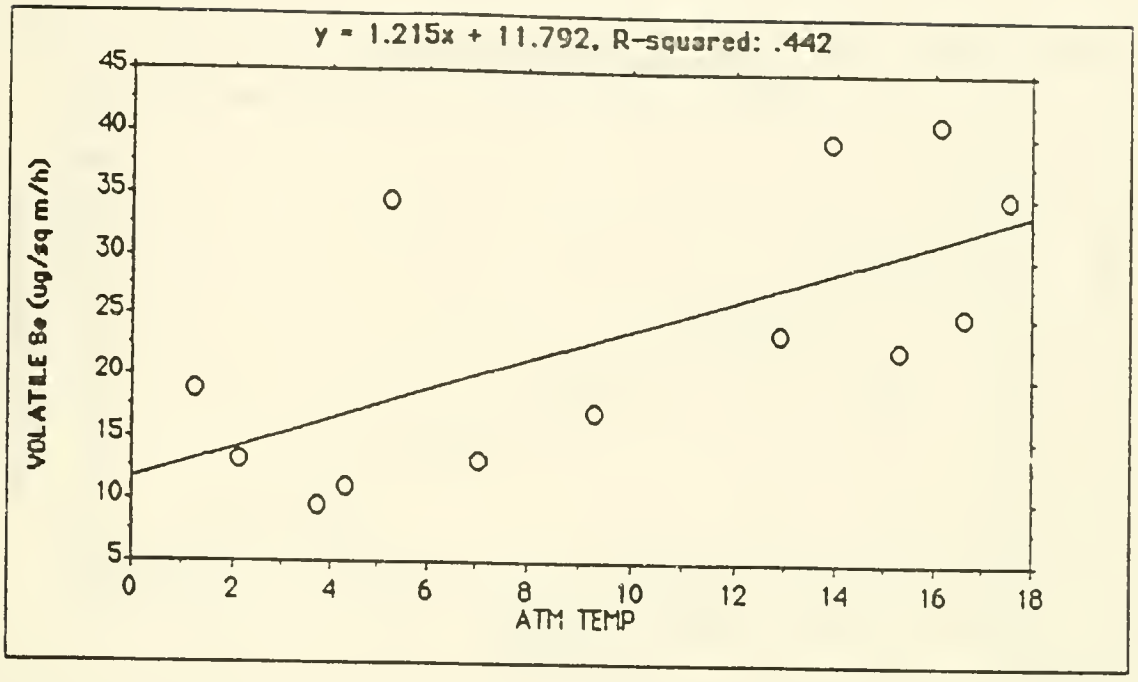


Fig. 3-36. Linear regression analysis of alkylselenide production in plot 57 and atmospheric and soil temperature.

PLOT 58



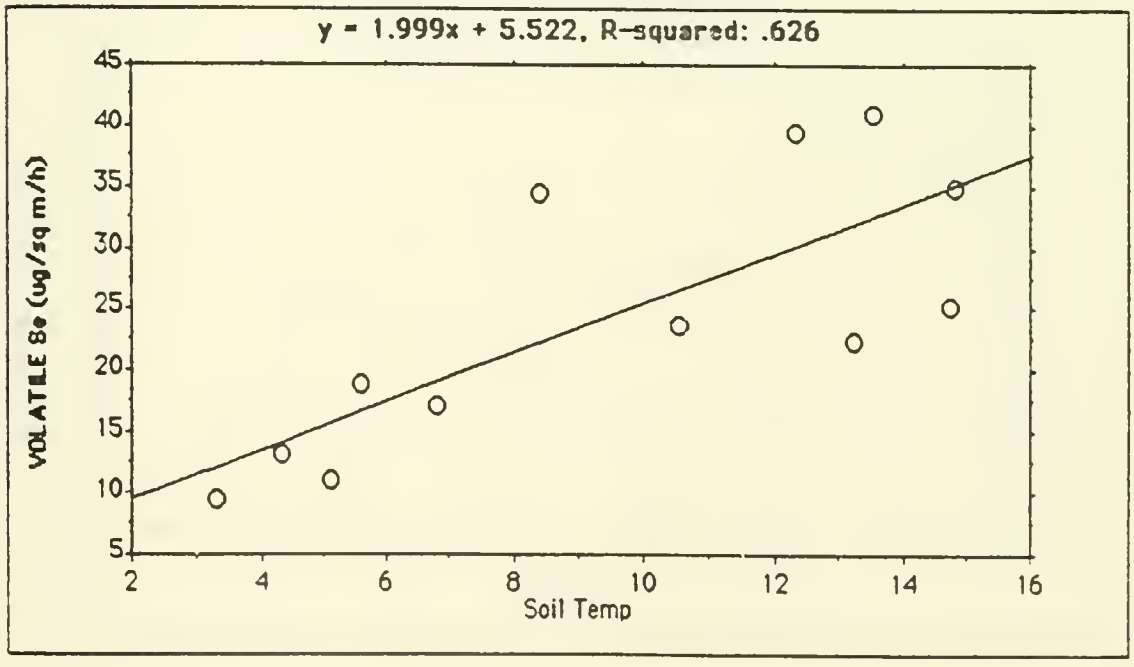
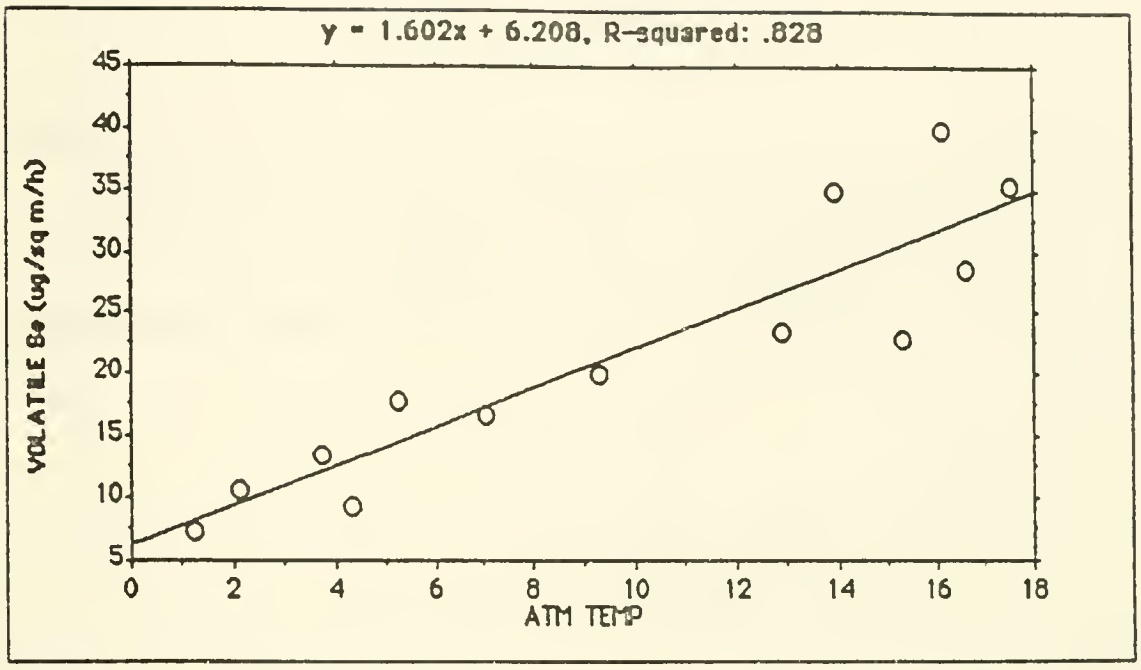


Fig. 3-37. Linear regression analysis of alkylselenide production in plot 58 and atmospheric and soil temperature.

PLOT 61



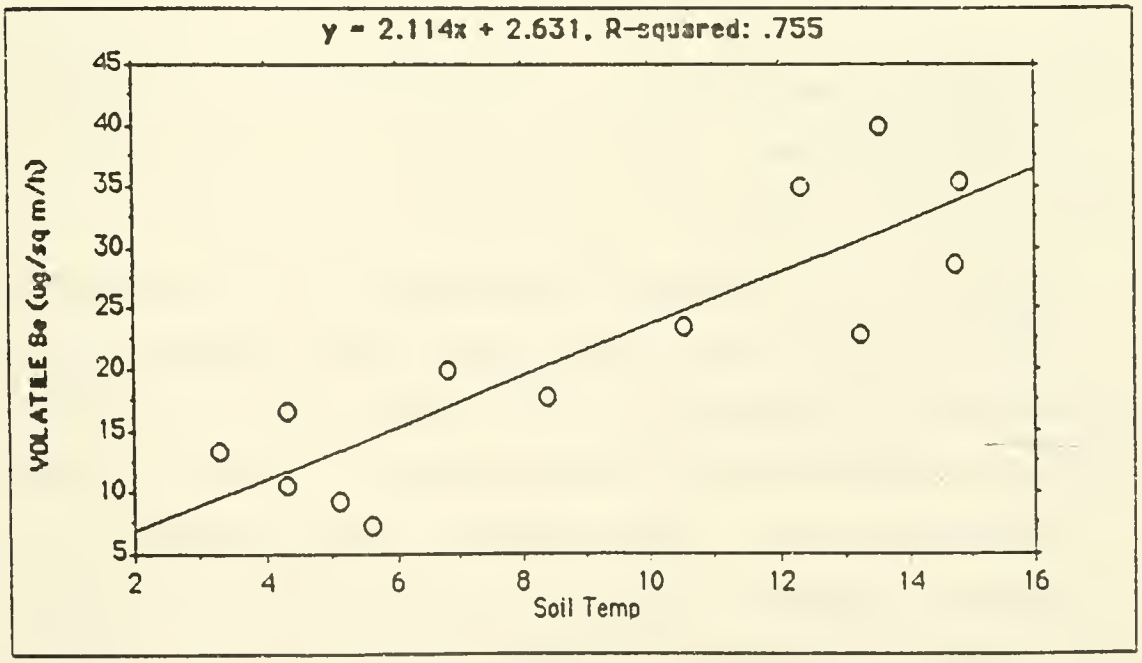


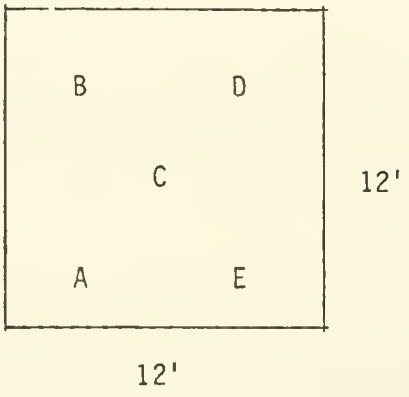
Fig. 3-38. Linear regression analysis of alkylselenide production in plot 61 and atmospheric and soil temperature.

CHAPTER 4

SOIL ANALYSES

Procedure

On July 29, 1987 five soil subsamples were collected to account for spatial variability within each plot. The samples were spaced approximately 3' apart from each other as shown below:



Soil samples were collected with a 2" diameter probe to a depth of 6" (the same depth as the rototiller mixes soil). An initial inventory of the Se content in soil profiles was also taken to a depth of 2' at 6" intervals before the application of amendments. Upon collection, each of the samples was placed in zip-lock bags, labeled and packed with blue ice in an ice chest. Once the samples were collected, the chest was delivered to CSUF along with the chain-of-custody forms. All chain-of-custody records are on file at UCR. The entire soil sample was passed through a 2-mm sieve and ground to 100-mesh. After the sample was thoroughly mixed, splits were mailed to UCR for analysis.

All samples were kept refrigerated at 4°C. The appendix provides the soil digestion procedure (EPA Method 3050) and analytical method (EPA Method 270.3) for determination of Se content (EPA Methods for the Chemical Analysis of Water and Waste, EPA 600/4-79-020). Modifications of the above approved method, together with methods developed at UCR are also documented in the Appendix. Samples were analyzed by atomic absorption spectrometry/hydride generation and reported on a dry weight basis.

Quality Assurance Objectives for Measurement of Data

The data quality objectives for this study are summarized in the folowing table.

Table 4.1. Data quality objectives

Data Quality Objective	How Determined	QA Plan Section	Criteria
Accuracy	Reference material	11.1	±20% of value if result is greater than 20 times CRDL; ± 4 times CRDL value if result is less than 20 times CRDL
Accuracy	Recovery in spiked sample	11.3	80-120% of recovery
Precision	Duplicate analysis of sample	11.2	15% if over 20 times CRDL; 20% if 5 to 20 times CRDL; ±1 CRDL if less than 5 times CRDL
Completeness	Number of samples analyzed	14.3	20-100% of samples
Representa-tiveness	Analyze reference materials	11.1	See criteria for accuracy.

Data Quality Objective	How Determined	QA Plan Section	Criteria
Comparability	Split samples also analyzed by UCR laboratory	11.2	See criteria for precision.
Detection limit	Lowest concentration level that can be determined to be statistically different from a blank	9.2.1	1 µg/L gas sample (DMSe, DMDSe) 0.1 mg/kg soil This is well below the level currently accepted by Fish and Game as the action level of 4 ppm in soil.

Internal quality assurance samples (USBR sediment standard reference samples) were analyzed to assure accuracy of our analytical technique. UCR participated in this program with the use of ICP and AAS. Both analyses using the two instruments were in a comparable range to that reported by USGS, LBL and CSUF (Table 4-2).

Among the split samples, UCR and CSUF did not initially agree in their results on Se content of the soil samples collected at Kesterson. UCR consistently had higher numbers, averaging 40% greater in Se content. Although the numerical values were consistently higher by UCR, both laboratories showed parallel trends in magnitude. In-house checks among the laboratories were determined to find the resulting differences in absolute numbers. The difference was attributed to the means of processing the soil, extraction procedures and use of analytical instruments. At that time, UCR was using an ICP while CSUF was using an AAS/hydride generation system. Also UCR was extracting their samples with HNO_3 for 3 days while CSUF carried out this process for 24 h. Both laboratories are

Table 4-2. Analysis of internal quality assurance samples to assess accuracy of analytical technique.

U.S. BUREAU OF RECLAMATION
SEDIMENT STANDARD REFERENCE SAMPLES

SRS ID	USGS[1]	LBL[2]	CSUF[3]	UCR-ICP[4]	UCR-AAS[5]
	mg/kg				
KS-1-S (306)	63	58	53	58 (RPD = 2.7%)	56 (RPD = 13.2%)
K-3-S (307)	85	87	82	94 (RPD = 2.8%)	82 (RPD = 5.46%)
K-6-S (308)	22	24	19	21 (RPD = 3.2%)	19 (RPD = 2.04%)
KS-12-E (309)	2.5	4.2	2.5	2.1 (RFD = 4.8%)	2.7 (RPD = 2.21%)

[1]Analyzed by the U.S. Geological Survey Laboratory Geologic Division. Results are based on the analysis of ten randomly selected splits from each standard using atomic absorption-hydride generation techniques.

[2]Analyzed by Lawrence Berkeley Laboratory three times each using X-Ray Fluorescence techniques.

[3]Analyzed by California State University of Fresno using atomic absorption-hydride generation techniques.

[4]Analyzed by University of California, Riverside using inductively coupled Argon Plasma Emission Spectrometry (4 replicates).

[5]Analyzed by University of California, Riverside using atomic absorption-hydride generation techniques (3 replicates).

now using the same extraction procedure (see Appendix for adapted procedure) and the same type of analytical instrument (AAS) to determine the Se content. Incidentally, these differences are most likely the cause of such discrepancies in quantitation of trace elements among other laboratories.

Results:

Split samples obtained from CSUF now show excellent agreement with results of UCR (Table 4-3). Samples collected from Ponds 4 and 11 were analyzed in duplicate with RPDs reported in Table 4-2. Selenium content among the samples ranged from 2.25 to 86.5 mg/kg. Among all of the samples analyzed, the average pool from both laboratories were 26.33 mg/kg (UCR) and 24.50 mg/kg (CSUF).

Soil samples are collected on a monthly basis (when weather permits). Such an interval was selected to observe a significant drop in Se content on a long term basis. The initial profile samples collected by LBL are currently being analyzed by CSUF. Although the results are incomplete, it appears that most of the Se is within the upper 6" of the soil profile (Figs. 4-1 to 4-4). Some subplots have considerable Se content within the 6-12" depth. Plots 52 and 53 had 3.1 and 6.0 mg/kg of Se at this depth, respectively. As much as 3.14 mg/kg of Se was found at 12-18" in plot 53.

In November and January of 1987, we decided to collect more profile samples in pond 4 because of a rising water table. We were concerned that the rising water would transport the soluble Se deep in the profile to the surface within our plots. Currently the east end of our plots (pond 4) are saturated with water and in some places under water. CSUF has not yet completed the analyses of these samples.

Table 4-3. Quality control of soil samples from Kesterson.

PROJECT: KESTERSON SELENIUM STUDY
DATE: February 12, 1988
SAMPLE SET: Check on CSUF
ANALYZED BY: David Thomason, UCR

Site ID	Sample ppm	Duplicate ppm	RPD* %	UCR Average ppm	CSUF Average ppm
POND 11					
K_1C_4	3.84	3.97	3.32	3.91	3.48
K_2C_4	6.46	6.26	3.14	6.36	5.62
K_4C_4	2.10	2.29	8.65	2.20	3.92
K_6C_4	4.48	5.00	10.97	4.74	3.93
K_8C_4	5.46	5.43	0.55	5.44	5.03
$K_{10}C_4$	3.72	4.10	4.85	3.91	3.26
$K_{12}C_4$	4.95	5.16	4.15	5.05	4.71
$K_{14}C_4$	3.68	3.48	5.58	3.58	3.50
$K_{16}C_4$	4.90	4.87	0.61	4.89	3.62
$K_{18}C_4$	3.24	2.96	9.03	3.10	2.48
$K_{20}C_4$	3.26	3.14	3.75	3.20	3.53
$K_{22}C_4$	2.99	2.96	1.00	2.98	3.15
$K_{24}C_4$	2.32	2.25	3.06	2.29	2.25
$K_{26}C_4$	2.75	2.58	6.37	2.66	2.37
$K_{28}C_4$	3.80	4.22	10.47	4.01	3.88
$K_{30}C_4$	4.46	5.26	16.46	4.86	4.16
				Avg: 3.95	3.68

RPD = relative percent difference [2(A-B)/A+B] * 100%.

Table 4-3. (continued)

PROJECT: KESTERSON SELENIUM STUDY
DATE: February 12, 1988
SAMPLE SET: Check on CSUF
ANALYZED BY: David Thomason, UCR

Site ID	Sample ppm	Duplicate ppm	RPD* %	UCR Average ppm	CSUF Average ppm
POND 11					
$K_{51}C_4$	17.09	16.95	0.82	17.02	21.42
$K_{52}C_4$	66.04	70.81	6.97	68.42	51.24
$K_{53}C_4$	41.20	41.03	0.41	41.11	41.17
$K_{54}C_4$	25.85	30.07	14.66	27.96	28.38
$K_{55}C_4$	81.60	86.92	6.31	84.26	86.50
$K_{56}C_4$	94.20	100.24	6.21	97.22	86.06
$K_{57}C_4$	61.44	59.31	3.52	60.37	51.83
$K_{58}C_4$	35.54	29.59	18.12	32.55	39.88
$K_{59}C_4$	31.55	30.82	2.37	31.18	30.28
$K_{60}C_4$	28.02	29.32	4.53	28.67	26.34
$K_{61}C_4$	46.40	39.22	16.77	42.81	40.97
$K_{62}C_4$	62.16	64.03	2.96	63.09	61.02
$K_{63}C_4$	54.19	58.12	6.99	56.15	48.28
$K_{64}C_4$	43.74	42.19	3.60	42.96	35.42
$K_{65}C_4$	55.72	54.04	3.06	54.88	47.00
$K_{66}C_4$	30.43	31.09	2.14	30.76	29.51
			Avg:	48.71	45.33

RPD = relative percent difference [2(A-B)/A+B] * 100%.

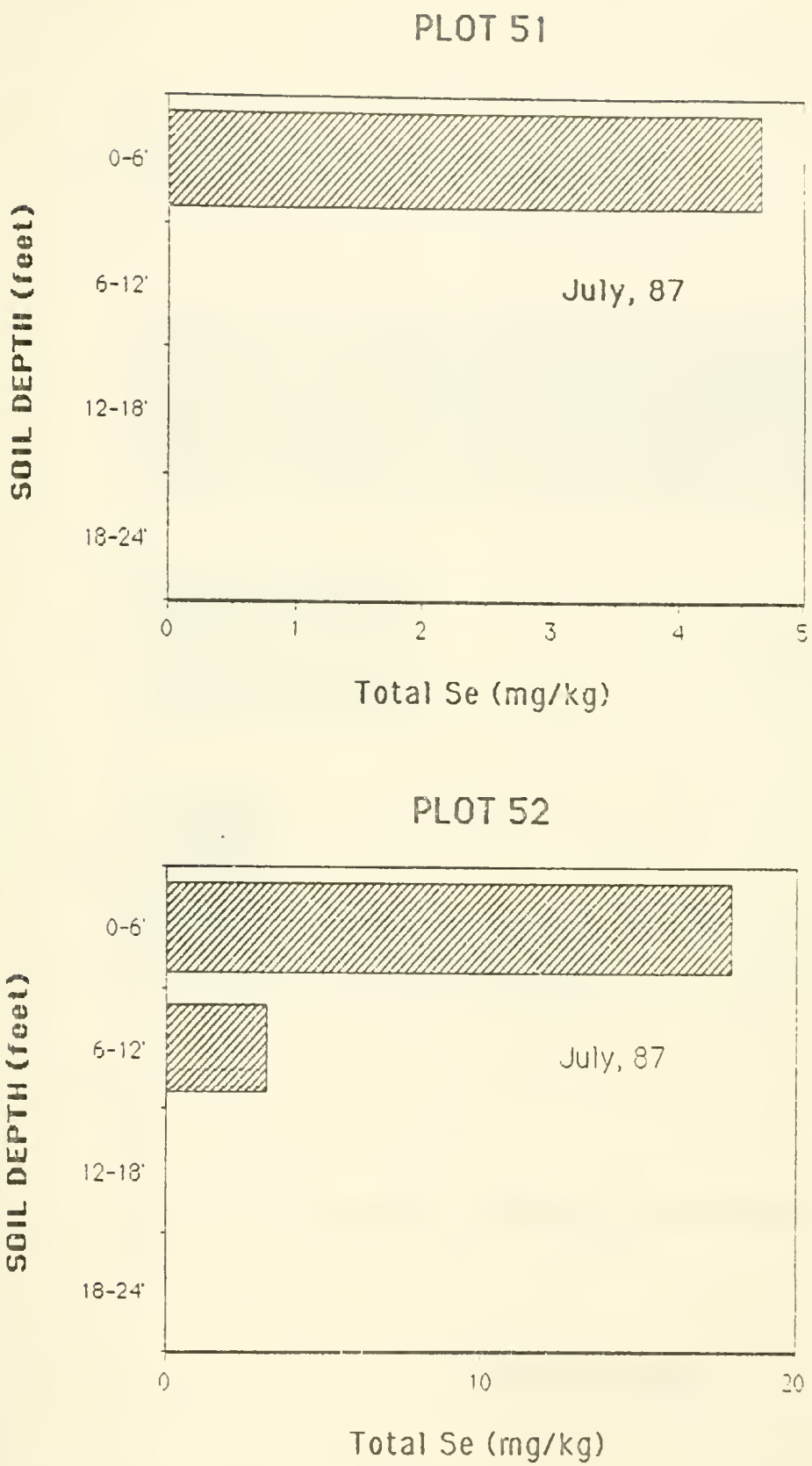


Fig. 4-1. Profile distribution of selenium in plots 51 and 52.

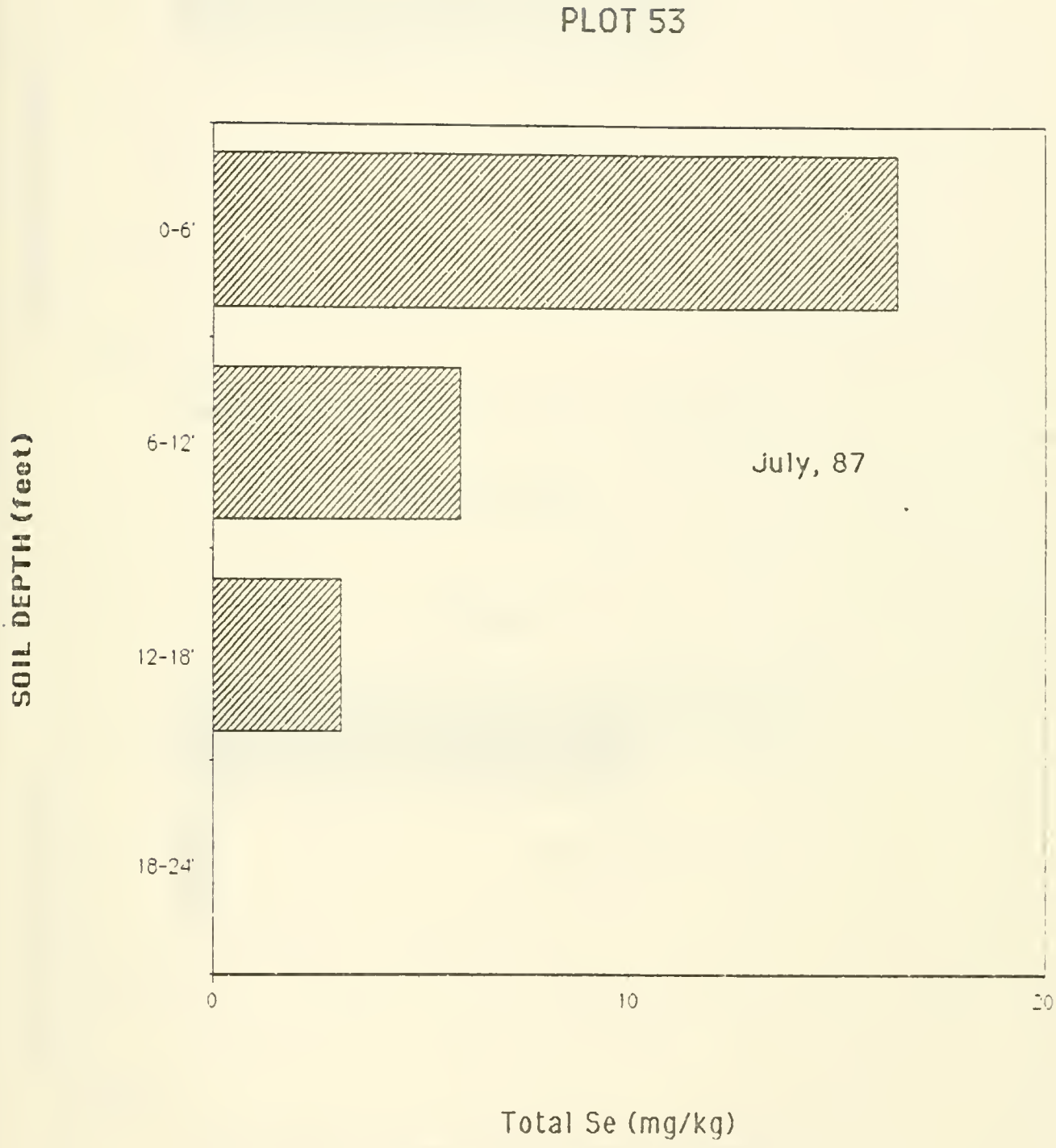
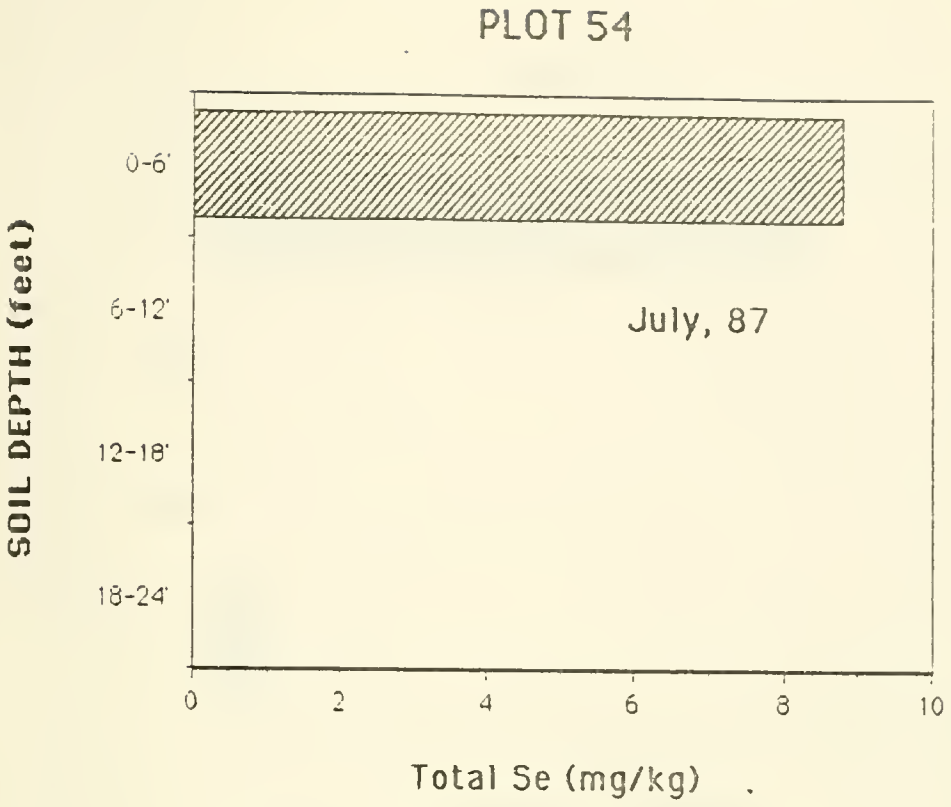


Fig. 4-2. Profile distribution of selenium in plot 53.



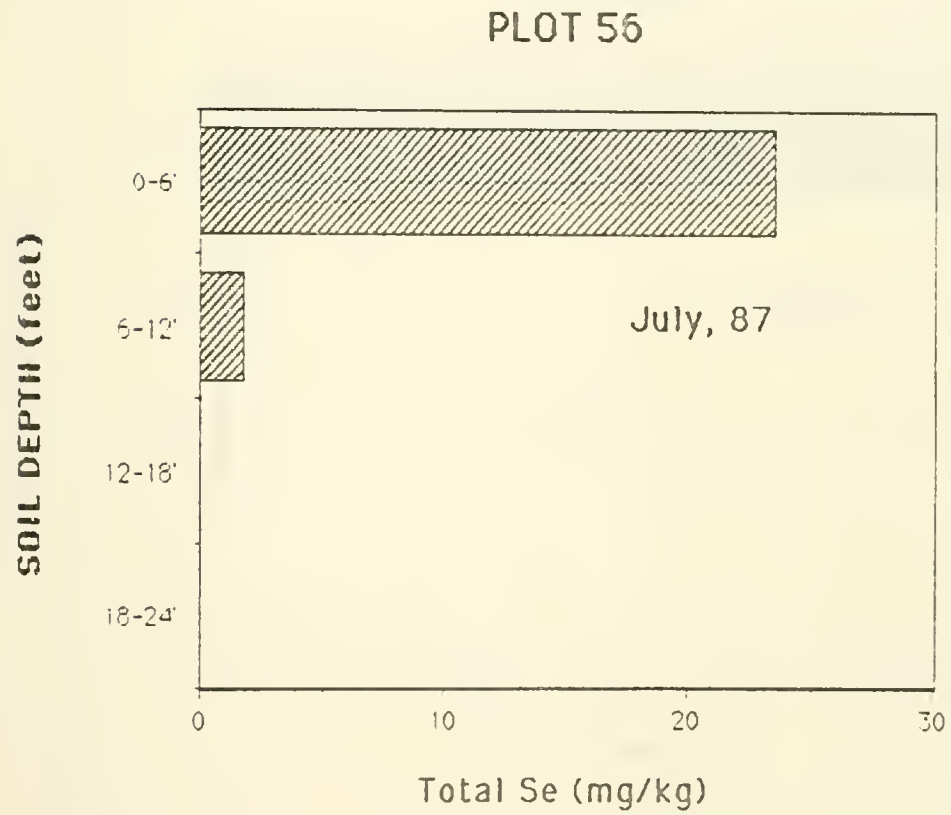


Fig. 4-3. Profile distribution of selenium in plots 54 and 56.

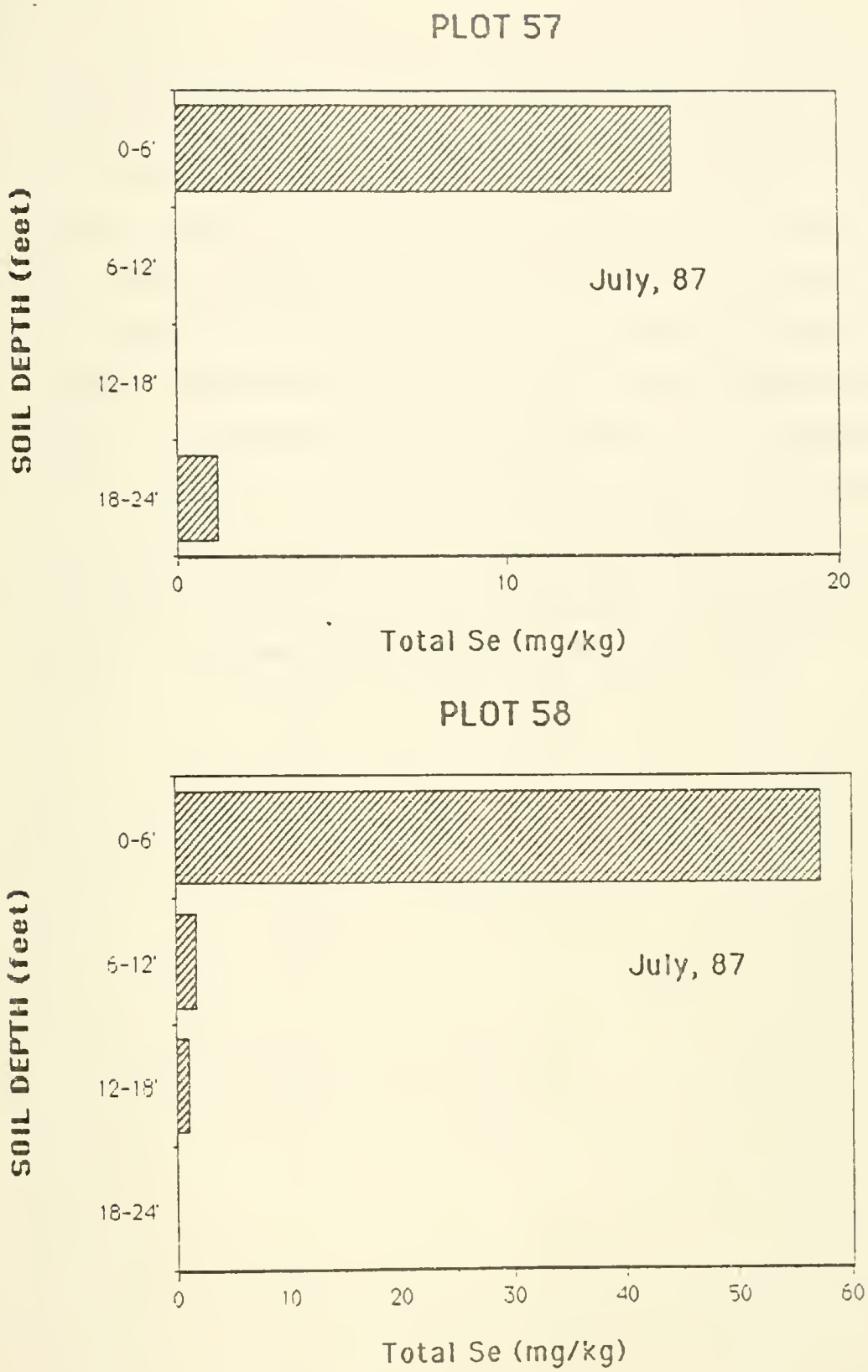


Fig. 4-4. Profile distribution of selenium in plots 57 and 58.

The inventory Se content in Pond 4 ranged from 10 to 209 mg/kg soil. The average of the pool values was 50.1 mg/kg with a median of 38.5 mg/kg. Data is incomplete on Pond 11, but of that collected, the average pooled data is 4.05 mg/kg with a median of 3.61 mg/kg. Figure 4-5 gives a perspective of the variability of the Se content in each of the subplots. To illustrate this, the Se content in subplot 56 varied from 39 to 209 mg/kg within 6 feet of each other. Higher Se content seems to be associated where water accumulates in low depressions on site. Variability is much more evident in Pond 4 when compared to Pond 11. Because of this variability, it makes it very difficult to extrapolate a decrease in Se levels on a short term basis. The movement of soil after rototilling also contributes to this variability.

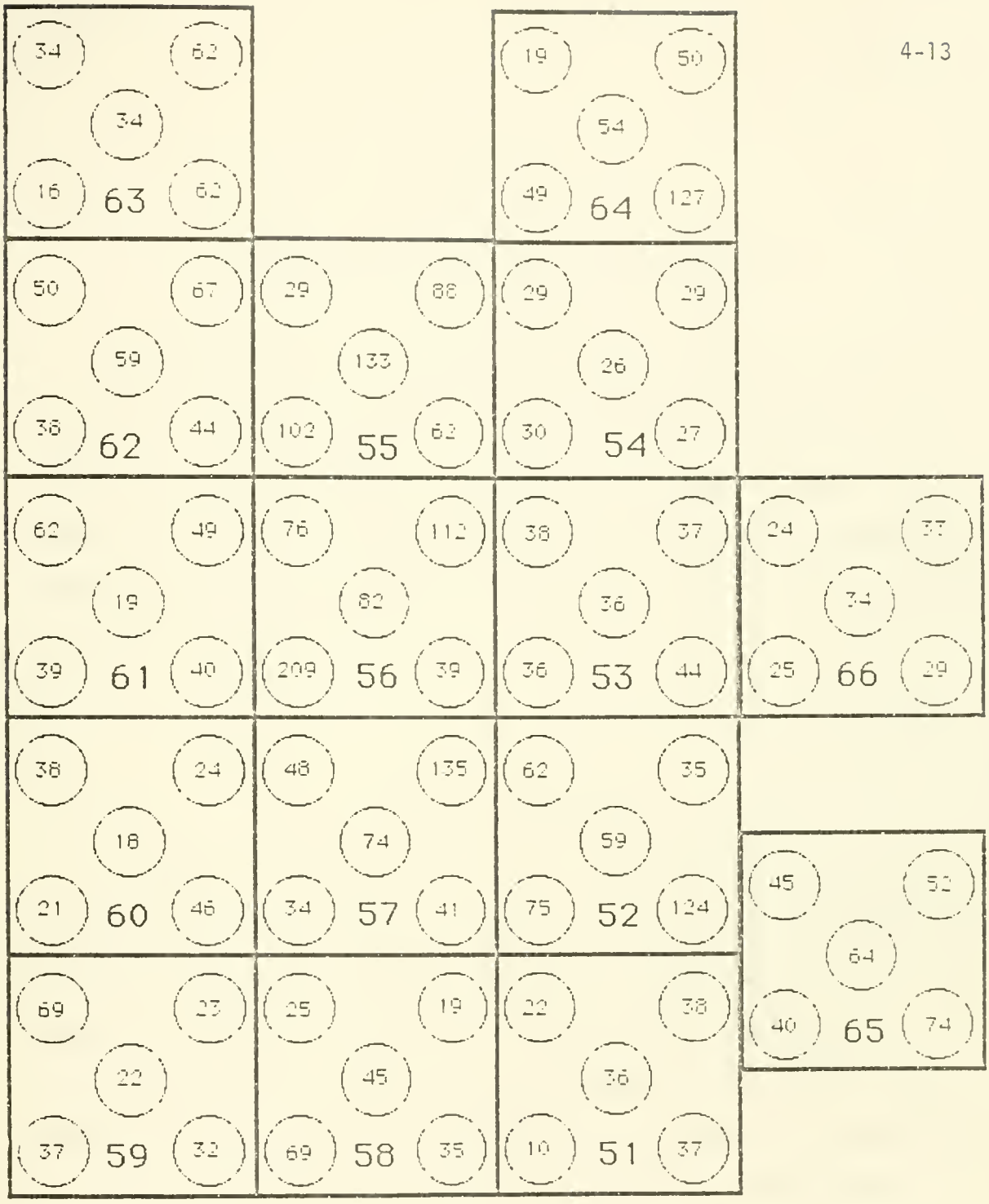


Fig. 4-5. Spatial variability of selenium content in the upper 6 inches of pond 4.

Chapter 5

POTENTIAL FOR Se REMOVAL BY VOLATILIZATION

A laboratory study was conducted to investigate the long-term incubation of Se-contaminated soils under controlled conditions. The importance of Se level for sustained volatilization rates was investigated, and the possibility of a minimal soil Se threshold concentration was addressed. The effect of selenate [Se(VI)] versus selenite [Se(IV)] as the Se source was studied.

MATERIALS AND METHODS

Alkylselenide production was measured using labeled Se, activated carbon traps and a continuous flow system. The soils used throughout this study (Table 5-1) were air-dried surface samples (0-15 cm) of Los Baños clay loam (fine montmorillonitic, thermic Typic Haploxeralf), Panoche clay loam (fine-loamy mixed, calcareous, thermic Typic Torriorthent), Panhill clay loam (fine-loamy, mixed, thermic Typic Haplargid), and Ciervo clay (fine montmorillonitic, calcareous, thermic Typic Torriorthent) that had been collected from Se problem areas. Ten-g soil samples were maintained at approximately -33 kPa (2.5 pF) and incubated at room temperature.

Table 5-1. Properties of the soils used.

	Los Baños	Panoche	Panhill	Ciervo
pH	7.96	8.05	7.81	8.13
Organic C, g kg^{-1}	9.67	9.77	8.34	4.71
Total N, mg kg^{-1}	957.6	980.6	667.4	647.3
Total Se, μg kg^{-1}	693.7	100.0	330.1	3.6
% clay	42.5	47.5	37.5	57.5
% sand	5.7	3.1	10.6	2.8

To study the effects of Se speciation and of Se concentration, Se was added as Na_2SeO_3 or Na_2SeO_4 at 0.01 to 1000 mg kg^{-1} soil, with a label activity of 0.5 mCi kg^{-1} soil. Na_2SeO_3 and Na_2SeO_4 were analytical grade (Alfa Products, Danvers, MA). $Na_2{}^{75}SeO_3$ and $Na_2{}^{75}SeO_4$ (radionuclide purity >99%) was obtained from Amersham (Arlington Heights, IL). The speciation of the two nonlabeled Se reagents was confirmed to be >99.9% correct by single-column ion chromatography. The speciation of the two labels was tested by paper chromatography. The fraction of $^{75}Se(IV)$ in the $^{75}Se(VI)$ label was <0.5%, that of $^{75}Se(VI)$ in the $^{75}Se(IV)$ label was <9.5% of the total ^{75}Se. All experimentation was performed in triplicate. Blanks were included for background determination. Trapping of alkylselenides began immediately after application of Se. Traps were sampled at 3.5-day intervals (unless noted otherwise) and counted directly in a gamma counter.

To study the effect of carbon on Se alkylation, dissolved pectin was added to the respective samples at 2 g C equivalent kg^{-1} soil. Pectin had been described as the most effective C amendment in an earlier study. Pectin applications were repeated every 35 to 45 days, when alkylselenide production had leveled off.

RESULTS

Volatilization rates for added Se(IV) (Fig. 5-1) and Se(VI) (Fig. 5-2) were highly dependent on the level of Se substrate. In both

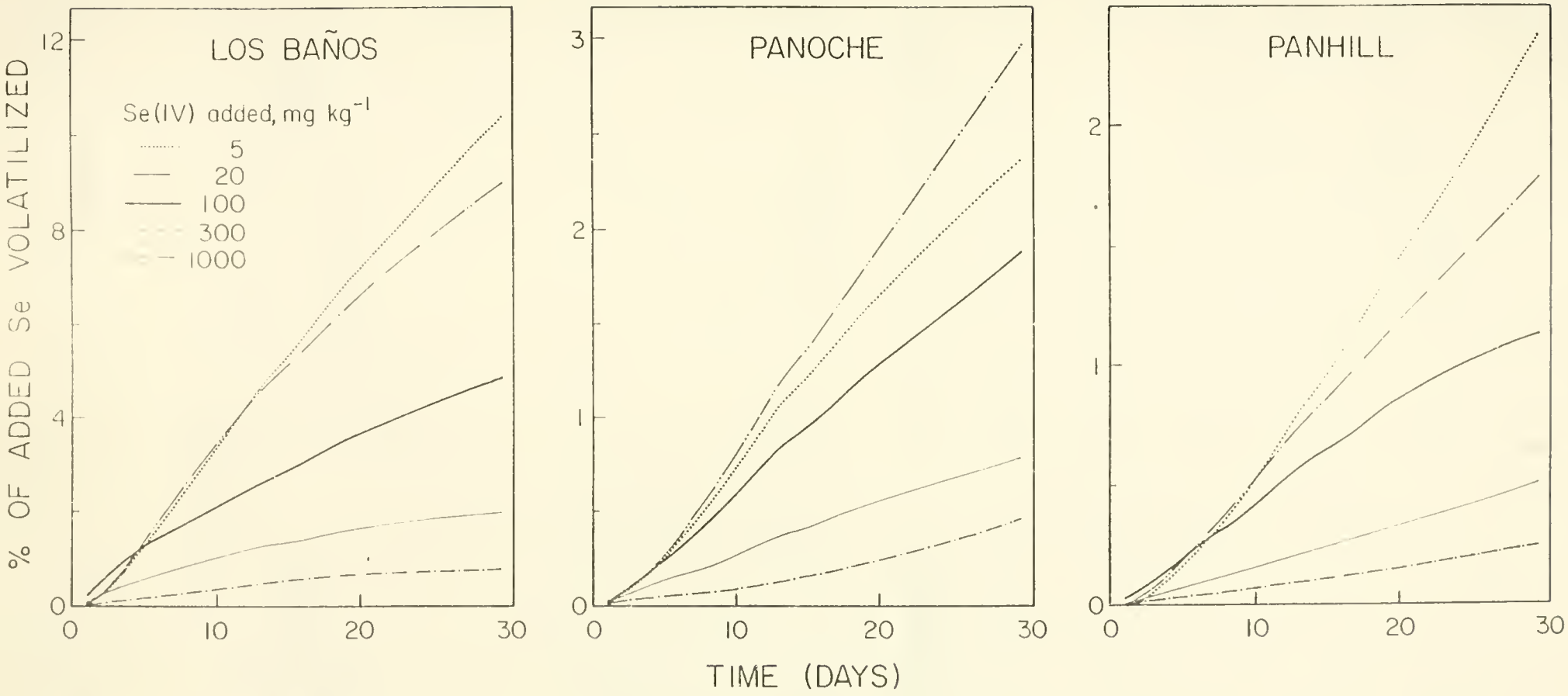


Fig. 5-1. Volatilization of Se(IV) added to Los Baños, Panoche and Pan-hill soils. No C addition. Sampling interval, 1.5 to 3 days.

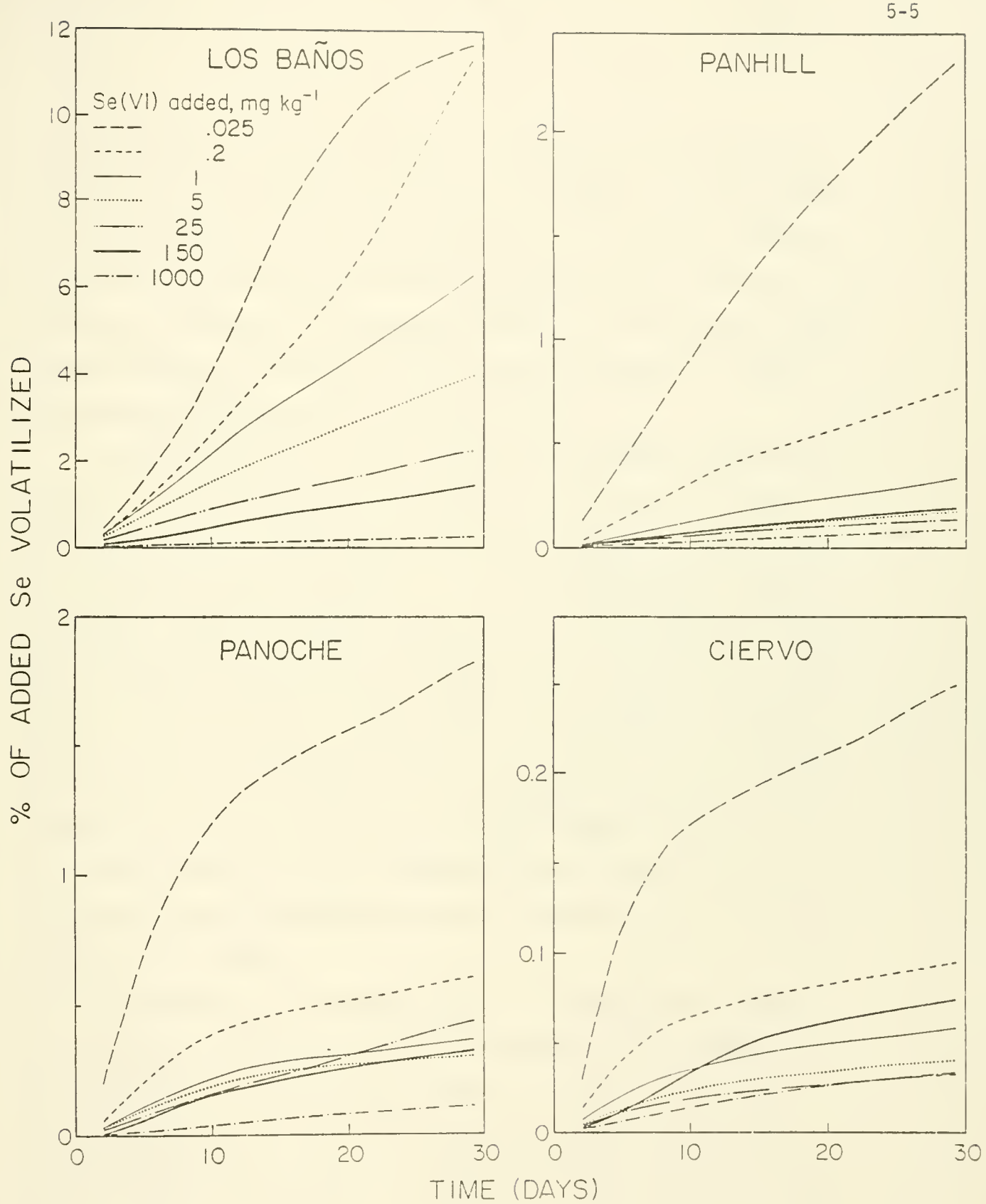


Fig. 5-2. Volatilization of Se(VI) added to Los Baños, Panoche, Panhill and Ciervo soils. No C addition.

cases, the highest rates (expressed in % of added Se volatilized) were observed with the lowest Se addition. For Los Baños, e.g., the average daily Se evolution was 0.35% at 5 mg Se(IV) kg^{-1} and 0.03% at 1000 mg Se(IV) kg^{-1}. Alkylselenide production was substantially lower with Se(VI) as a substrate, when compared to Se(IV). Los Baños, e.g., only volatilized 0.13% of the added Se(VI) per day at 5 mg kg^{-1}. Similar relationships were observed with the other soils.

By amending the soils with a C source, the observed relationship between Se level and volatilization rates was reversed in Los Baños (Fig. 5-3). Over a period of 118 days the average daily volatilization was 0.20% with 0.02 mg Se(IV) kg^{-1} soil, and 0.44% with 25 mg Se(IV) kg^{-1} soil. This reversal was not observed with the low producing Ciervo soil. Panoche soil, which was the intermediate producer in the experiments without C amendment, had the highest volatilization percentages (0.38% day^{-1}) at 0.2 mg Se(IV) kg^{-1}, and lower rates at the higher and lower Se(IV) levels. Similarly, using Se(VI) instead of Se(IV) (Fig. 5-4), the strongest relative volatilization was observed at 0.2 and 1 mg Se(VI) kg^{-1} in Los Baños and Panoche, respectively, and at 0.04 mg Se(VI) kg^{-1} in Ciervo.

The addition of C narrowed the gap in Se evolution rates between the different soils, equally for Se(IV) and Se(VI). For example, without C addition at 5 mg Se(IV) kg^{-1}, 10.4% and 2.4% of the added Se were volatilized in 30 days by Los Baños and Panoche, respectively. With C amendment, the respective values were 18.5% and 10.4%. At 5 mg

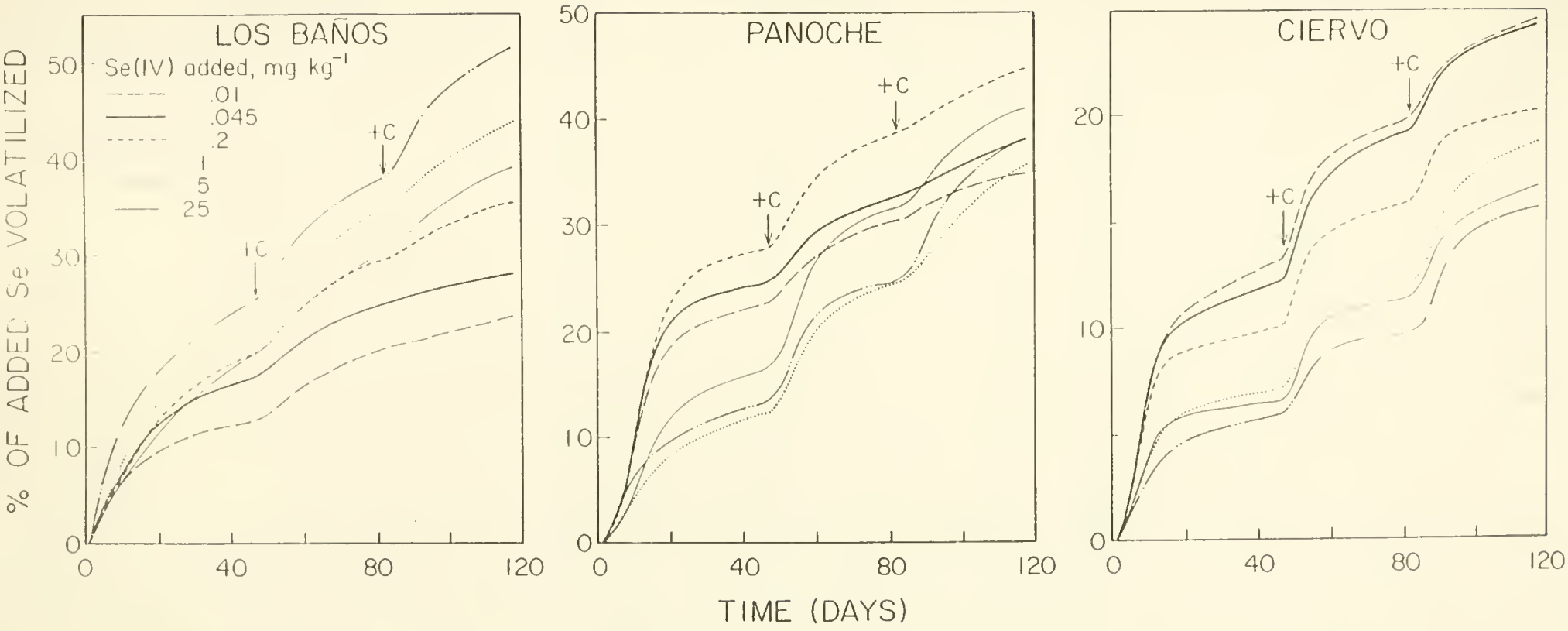


Fig. 5-3. Volatilization of Se(IV) added to Los Baños, Panoche and Ciervo soils. Equivalent C addition, 2 g kg^{-1}, repeated twice as indicated.

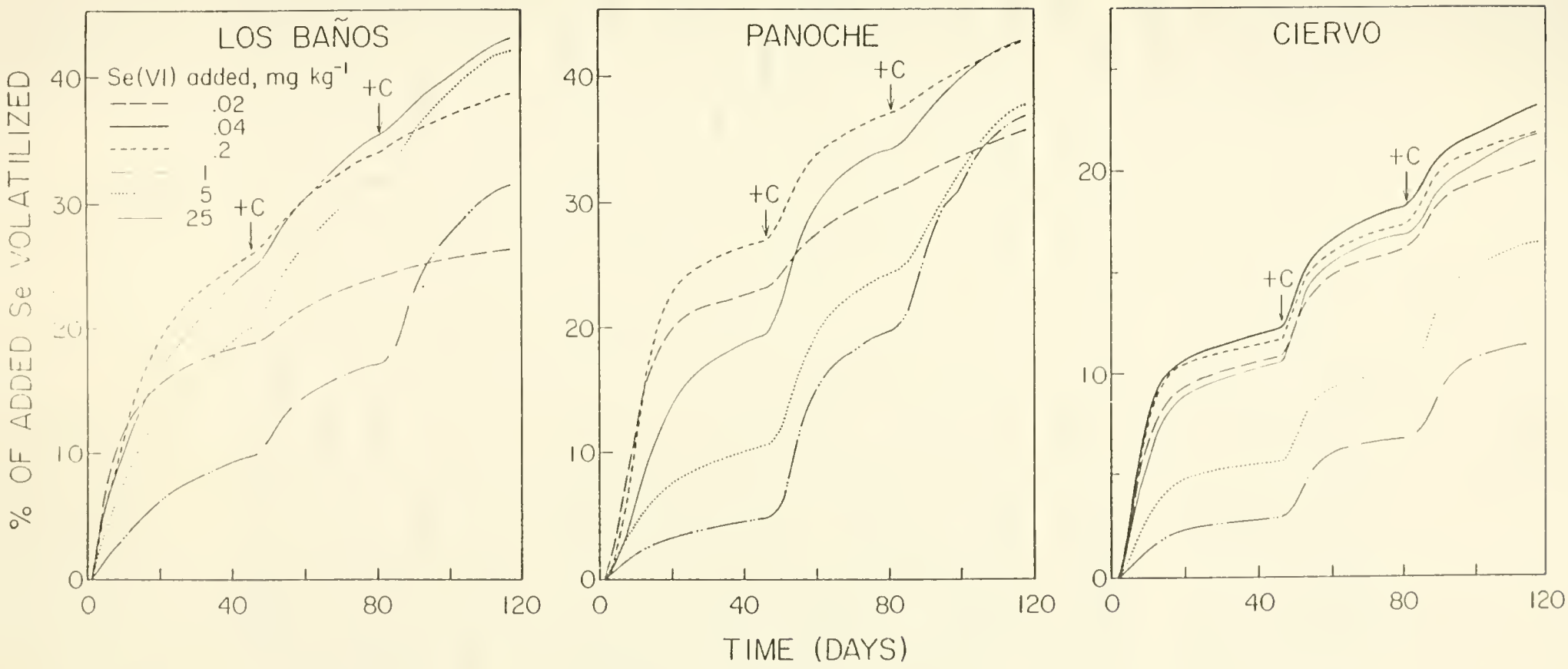


Fig. 5-4. Volatilization of Se(VI) added to Los Baños, Panoche and Ciervo soils. Equivalent C addition, 2 g kg^{-1}, repeated twice as indicated.

Se(VI) kg^{-1} without C, 4.0%, 0.3% and 0.04% of the added Se evolved from Los Banos, Panoche and Ciervo in 30 d, while 16.5%, 9.2%, and 5.3% was detected with C, respectively. These numbers also indicate that the rate differences in volatilization of Se(IV) versus Se(VI) almost disappear upon the addition of a C source.

Carbon amendments greatly accelerated volatilization rates in all cases. The acceleration was most pronounced with soils that showed lower alkylselenide production in their unamended state, and with Se(VI) as the Se source. The rate increasing effect disappeared within 35 to 45 days; however, it was observed again upon repeated C additions in most treatments. The response to repeated C amendments was stronger for the higher Se levels, in particular with Se(VI) as a substrate.

Comparing the average volatilization rate for the first 30 days in Figs. 5-1 through 5-4, C addition increased the rates 1.8-fold and 4.4-fold in Los Baños and Panoche, respectively, at 5 mg Se(IV) kg^{-1}. Adding Se(VI) to Los Baños, Panoche and Ciervo soils, the rates increased by 2.0-fold, 41.7-fold and 115.9-fold at 0.2 mg kg^{-1}, respectively; 4.2-fold, 30.6-fold and 131.5-fold at 5 mg kg^{-1}; and 3.6-fold, 9.3-fold and 78.3-fold at 25 mg kg^{-1}. As a result of these dramatic rate increases, substantial portions of the added Se were volatilized within a period of 118 days, with a total of 3 C applications. Those portions, depending on the soil, Se species, and Se level, ranged between 11.3 and 51.4%. The highest Se removal observed for Ciervo

soil was 23.0% at 0.04 mg Se(VI) kg^{-1}, 42.7% for Panoche at 1 mg Se(VI) kg^{-1}, 42.9% for Los Baños at 1 mg Se(VI) kg^{-1}, 24.4% for Ciervo at 0.02 mg Se(IV) kg^{-1}, 44.6% for Panoche at 0.2 mg Se(IV) kg^{-1}, and 51.4% for Los Baños at 25 mg Se(IV) kg^{-1}.

CONCLUSIONS

The observation that C amendments tend to eliminate the differences in the rates of methylation of Se among soils, is an indication that carbon is a limiting factor for this transformation. While the pathway has not been elucidated, we can suggest that it involves reduction of Se and transfer of carbon groups, hence requiring energy at the expense of the added carbon. The importance of a C supply is evident by the rapid experimental disappearance of the C amendments.

From the data presented here, one can postulate that there is no threshold concentration of soil Se below which volatilization would not occur. Even at extremely low Se levels, Se(IV) and Se(VI) were readily converted to volatiles, independent of C supplementation. This indicates that, with sufficient time, depletion of soil Se through volatilization would approach 100%, if there is no renewed Se input.

Evidence suggests that there is a potential for biovolatilization to remove Se up to 50% in 4 months. This was achieved under semi-optimized laboratory conditions, i.e., constant temperature (23°C) and

moisture content. On the other hand, the temperature was not at the optimum of $\geq$35°C, and metal activators, such as zinc, were not used in this laboratory study. Metal activators were shown earlier to increase volatilization rates up to 3-fold. A temperature increase from room temperature to 35°C would cause more than a 2-fold acceleration of this process (Q_{10} = 2.60). These factors, applied in the field, should at least partially outweigh the sub-optimum moisture situation in the field plots.

CHAPTER 6

FIELD APPLICATION OF THE BIORECLAMATION PROGRAM

The major limiting factors in promoting biomethylation of Se in the field appear to be an available C source and moisture.

Carbonaceous Materials

Inquiries were made to local business establishments within the vicinity of Kesterson that could provide carbon materials to be incorporated into the seleniferous soil. The transport of these materials is the major expense. The source, availability and costs of these materials are listed in Table 6-1.

Tomato pomace, which has 3% total pectin content per dry weight (but has many other polysaccharides that enhance biomethylation of Se) is readily available near Kesterson. Canneries in Los Baños, Tracy, Stockton and Merced, CA, currently have tomato pomace hauled away as a waste product at the cost of shipping. The processed material is dried and used as cattlefeed. Inogomar Packing in Los Baños deals with volumes of 50 t/day during the high season (July-October). An estimated cost of hauling tomato pomace to Kesterson by R. C. Buggs Trucking, Fresno, was $7/ton from all the localities mentioned above.

Another source of carbon would be melons such as canteloupe and honeydews. There are two packing houses in Los Baños which handle melons and have waste during their shredding operation. It was suggested by Namm Packing, Los Baños, that residual melons in the field which are

Table 6-1. Cost of management practices for the bioremediation program

Source	Material	Available	Costs
Inogomar Packing Richard Rostomily (209) 854-2444	tomato pomace process 50 t/day	July-October	$7/ton*
Tri-Valley Growers, Los Baños David Brown (209) 826-1970	tomato pomace	July-Ocober	$7/ton*
Heintz Canneries, Tracy, Stockton	tomato pomace	July-October	$7/ton*
Ragu, Merced	tomato pomace	July-October	$7/ton*
Del Monte, Stockton	tomato pomace	July-October	$7/ton*
Hauler, R. C. Buggs (209) 836-5911 (209) 233-4397	8 trucks 30 trailers	any season	$5-7/ton* (includes loading)
Namm Packing Aldo Sansoni (209) 826-4210 (209) 826-4665	melons (cantaloupe, honeydew (harvest residual in field)	July-October	$35/ton (includes loading and delivery)
Lindemann Packing George Lindemann (209) 826-1076 main office: (209) 826-2442	melons	July-October	

*result of only transport cost

Table 6-1. (continued)

Source	Material	Available	Costs
CCP_i	citrus peel	November-May Feb-October	$4/wet ton + $11/ton freight (total=$15/ton)
Sunkist, Tipton	citrus peel	November-May Feb-October	$5-7/wet ton freight=$10.50/ton (total=$15.50 to $17.50/ton)
Gallo	grape pomace apple,pear,grape pomace (wet)	year around	$20-$30/wet ton (includes delivery)
Harris Ranch	cattle manure	spring and summer	$20/ton incl. freight $3/ton to spread
Rain for Rent	irrigation equipment:		
	a) field equipment (lateral pipeline, risers, mainline, pumps)		$395,240
	b) automation of in-field operations		$ 77,400
	c) automated moisture sensing equipment		$ 92,200
	d) installation labor		$ 50,000
	e) contingencies		$ 25,000

not harvested could also be recovered and hauled to Kesterson. This could contribute to a relatively large tonnage of melons to apply in the bioremediation program.

Citrus peel and grape pomace could also be incorporated into the seleniferous soil. Citrus peel (Albedo) has a relatively high pectin content, 30-35% as dry weight. The major expense of these materials would be freight. The wet tonnage would cost approximately $4 to $7/ton plus freight ($11/ton).

Sugarbeet pulp is also an excellent source of pectin (15-20% dry weight) which is currently selling as cattlefeed for about $15/wet ton. If available, this material could be used as a readily decomposable C source.

Cattle manure has been demonstrated to promote methylation of Se in the field. The quoted price from Harris Ranch is $20/ton which could be furnished in the spring and summer months. Additional costs of spreading was quoted at $3/ton.

Many of these carbonaceous materials could be applied with a spreader truck for light loads within the N ponds. For heavier loads applied to the S ponds, a drag scraper would most likely be required. On a long term basis, the addition of C sources would not only promote the biomethylation rection as a remedial process to remove Se, but also promote the fertility of the treated soil. Incorporation of these materials would lead to greater buffering capacity, cation exchange capacity, nutrients for plant growth, microbial diversity, water holding capacity, and granulation (soil structure), overall promoting this site to a very rich agronomic environment.

Irrigation

Moisture is a limiting factor in this bioremediation process, particularly in the summer months. Irrigation equipment quoted by Rain for Rent would cost approximately $500,000/500 acres including all pipes, pumps, automated operation, and moisture sensing devices (see Appendix B for details). The costs of field irrigation equipment could be reduced considerably upon a custom proposal.

Overall Cost

Considering the incorporation of one or several types of materials (tomato, citrus peel, grape pomace, and manure), the costs would range from $7 to $20/ton. If the entire reservoir was treated with 15 tons/acre in the N ponds (cells 7-12) and 30 tons/acre in the S ponds (cells 1-6), then the required tonnage for three applications (spring and two in the summer), assuming 500 acres will be treated, would be 22,500 tons in the N ponds and 45,000 tons in the S ponds with a total application of 67,500 tons. The cost of the material and transport would range from $472,500 to $1,350,000 (mid range = $911,250). Additional costs would be required for spreading and discing (mixing) the material into the soil, but this would be minimal compared to the actual cost of the transported amendments. With irrigation ($1.3 million) and periodic discing, the total cost of this operation would most likely be in the vicinity of $2-3 million/year. Since this remedial action may be long term, requiring 2 to 3 years for complete Se removal, the total cost for such a project could possibly be in the $4-9 million range.

APPENDIX A

ANALYTICAL METHODS

ADDITIONS/MODIFICATIONS TO METHOD 3050

4.0 Apparatus and Materials

25 mm o.d. glass digestion tubes (100 mL capacity)

7.0 Procedure

7.1 Initial processing of soil sample

a. Thaw frozen soil sample and bring to room temperature.

b. Open sample container and air dry soil samples at ambient laboratory temperature for 24 hours. (Note: high moisture, "wet", soil samples will require longer drying times.)

c. Pulverize dried sample and sieve through 10 mesh (2 mm diam. holes) sieve. Remove organic material and rock material that does not pass sieve.

d. Mix sample well and remove approximately 25 g aliquot. Grind sample to pass 100 mesh sieve. Mix sample well.

e. Weigh and transfer approximately 0.5 g of soil to digestion tube.

7.2 Digest sample overnight (10-15 hours) at 70-75°C with 5 mL nitric acid and 5 mL distilled water.

7.3 Add 30% hydrogen peroxide (3 mL total) in small increments (to prevent foaming); digest for an additional 4-8 hours.

7.4 For hydride generation: Add 20 mL hydrochloric acid (4-6 M) and digest until frothing decreases. Then add additional 10 mL hydrochloric acid and digest overnight (10-12 hours). Cool and dilute to 100 mL. Use appropriate additional dilution of aliquot of digest to get within calibration range on atomic absorption instrument (10-50 µg).

METHOD 3050

ACID DIGESTION OF SLUDGES

1.0 Scope and Application

1.1 Method 3050 is an acid digestion procedure used to prepare sludge-type and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by AAS or ICP for the following metals:

antimony	cadmium	nickel
arsenic	chromium	selenium
barium	copper	silver
beryllium	lead	thallium
		zinc

1.2 Method 3050 may also be applicable to the analysis of other metals in slude-type samples. However, prior to using this method for other metals, it must be evaluated using the specific metal and matrix.

2.0 Summary of Method

2.1 A dried and pulverized sample is digested in nitric acid and hydrogen peroxide. The digestase is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Sb or the flame analysis of Sb, Ba, Be, Cd, Cr, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn or the flame analysis of Ag and Ti.

3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

4.0 Apparatus and Materials

4.1 125-ml conical Phillips' beakers
4.2 watch glasses
4.3 drying ovens that can be maintained at 30°C
4.4 thermometer that covers range of 0-200°C
4.5 Whatman No. 42 filter paper or equivalent

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): water should be monitored for impurities

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxide (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section 1 of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples will be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Weigh and transfer to a 125-ml conical Phillips' beaker a 1.0-g portion of sample which has been dried at 60°C, pulverized, and thoroughly mixed.

7.2 Add 10 ml of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample at 95°C and reflux for 10 min. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continueu to add 30% H_2O_2 in 1-ml aliquots with warming until tne effervescence is minimal or until tne general sample appearance is unchaged. (Note: Do not add more than a total of 10 ml 30% H_2O_2.)

7.5 If the sample is being prepared for the furnace analysis of Ag and Sb or direct aspiration analysis of Ag, Sb, Ba, Be, Cd, Cr, Cu, Pb, Ni, Tl, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type Ii water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 0.5% (v/v) HNO_3 and is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume, and any required reagent or matrix modifier, and analyze by method of standard additions.

8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition will be used for the analysis of all EP extrcts and whenever a new sample matrix is being analyzed.

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 2 *ug/l*

Preparation of Standard Solution

1. Stock Selenium Solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Approved for NPDES and SDWA
Issued 1978

Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides (> 800 mg/1) and sulfate (> 200 mg/1). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/1, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing < 2 ug/1 and spiked with a concentration of 20 ug/1, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 ug/1 level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 ug/1, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 ug Se/l, the standard deviations were ±0.6, ±0.4, and ±0.5, respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).

SELENIUM

Method 270.3 (Atomic Absorption, gaseous hydride)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

1. Scope and Application
   1.1 The gaseous hydride method determines inorganic selenium when present in concentrations at or above 2 *ug/l*. The method is applicable to drinking water and most fresh and saline waters, in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.
2. Summary of Method
   2.1 Selenium in the sample is reduced from the −6 oxidation state to the +4 oxidation state by the addition of $SnCl_2$. Zinc is added to the acidified sample, producing hydrogen and converting the selenium to the hydride, SeH_2. The gaseous selenium hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2–20 *ug/l* using the 196.0 nm wavelength.
3. Comments
   3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of selenium to establish adequate recovery.
   3.2 Organic forms of selenium must be converted to an inorganic form and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in method 206.5 (Standard Methods, 14*th* Ed. 404B, p 285, Procedure 4.1) should be used.
   3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
   3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
   3.5 Data to be entered into STORET must be reported as *ug/l*.
4. Precision and Accuracy
   4.1 Ten replicate solutions of selenium oxide at the 5, 10 and 15 *ug/l* level were analyzed by a single laboratory. Standard deviations at these levels were ±0.6, ±1.1 and ±2.9 with recoveries of 100, 100 and 101%. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low-Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA, vol 65, p. 731, Nov. 1973.)

Approved for NPDES and SDWA
Issued 1974

5. References

5.1 Except for the perchloric acid step, the procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 159, Method 301A(VII), (1975)

APPENDIX B

QUOTATIONS

estern oilfields supply co.
BOX 2248 BAKERSFIELD, CALIFORNIA 93303

rain for rent inc.
PHONE (805) 399-9124 TWX 910-327-1107 LAKECO

February 23, 1988

TO: Dr. Frankenburger
Dept. of Soil
Ext. 3405

FROM: Dave Jones

Dear Bill:

The following represents my best input on costing for the irrigation equipment and manure for a 500 acre job at Kesterson. These prices are firm from the suppliers of equipment and manure until September 1, 1988.

Doing all of Kesterson using your technique should not exceed $2,840,520 plus tax for all the equipment plus materials. This number anticipates that the Bureau of Reclamations would do the discing of the manure with existing manpower and equipment.

If the discing is to be done otherwise you need to add the cost of tractors, disc's, manpower and fuel to the cost on the 500 acres and/or all of Kesterson.

FIELD IRRIGATION EQUIPMENT $ 395,240.00

(Rental for one season - estimated six months)

Solid set aluminum irrigation equipment allows for rapid installation and removal. Designed to provide optimum application uniformity and therefore optimum control of soil moisture. Consists of standard open field sprinklers with galvanized steel risers on 3 inch aluminum lateral pipe. Connected to 10 inch aluminum mainline and tied into a portable self-contained diesel-driven pumping plant with filter.

NOTE: The current shortage of irrigation pipe due to the drought situation in California would require us to purchase new pipe for this project. Therefore, our prices reflect the current abnormally high price levels of materials from the manufacturer.

FROM WDSCO #14 8053936681 TUE 02.23.88 15:25 NO.28 PAGE 1

February 23, 1988

Dr. Frankenburger
Page 2

IRRIGATION AUTOMATION EQUIPMENT $ 77,400.00

(A purchase for the project)

Automation of the irrigation system is designed to provide manual infield operation, automatic (computer) at-site operation or remote (phone) operation of the system. This system will also provide past history of valve operations and current status of valve operations. This system consists of standard electric, field solenoid valves hardwired to field satellites. These field satellites are in turn connected to the computer system via a standard communication cable. Data and control from the computer to automation system is via a standard RS 232 port. This system utilizes a standard IBM-AT/compatible configuration with printer and optional modem.

AUTOMATED MOISTURE SENSING EQUIPMENT $ 92,200.00

(A purchase for the project)

This system is designed to provide for accurate field measurement and monitoring of soil moisture conditions. This is for the threefold purpose of maintaining optimum moisture conditions for the growth of fungi, to insure that saturation does not occur and to check that deep percolation does not occur. The equipment includes automatic transmitting soil moisture sensors hardwired to field transceivers. These field stations are powered by battery with solar charging and transmit field sensor data to a base station. This base station in turn transmits the data to the computer via a standard RS-232 port. The data provided includes both soil moisture status and maintenance status of the soil moisture sensors.

UNFORESEEN INCIDENTALS/CONTINGENCIES $ 25,000.00

INSTALLATION LABOR $ 50,000.00

February 23, 1988

Dr. Frankenburger
Page 3

MANURE	$ 297,000.00
(Includes trucking)	

15,000 tons delivered in two quantities. 7,500 tons at the start of spring and 7,500 tons in midsummer to Kesterson Reservoir. Each delivery will take 4 days to complete.

TOTAL COST FOR 500 ACRES	$ 936,840.00

The above does not anticipate any special clothing, aspirator or shower requirements for operators or workers involved in risky environmental conditions, nor does it include long distance pipelines to supply the system with water.

The manure can be spread for an additional cost of $3.00 per ton on relatively smooth ponds. Very rough terrain would increase the cost of spreading.

All prices include freight to Kesterson Reservoir but do not include state or federal taxes that may be charged. The above also does not include fuel costs for the diesel pump. This would cost $8.00 to $10.00 per hour of operation. You should anticipate this cost as an addition to your estimate.

It may be possible to reduce the cost of the rented field irrigation equipment. To accomplish this we would need to make exact measurements of the site and layout the sprinkler system on the basis of a custom proposal. An odd shaped pond might require more pipe, so the price could increase.

I hope this is of help to your project! You can be confident with these numbers, so go get this $25-50 million dollar bill at Kesterson reduced to something more logical like the above.

Best Regards,

Dave Jones /ek

Dave Jones

stern oilfields supply co.
OX 2248 BAKERSFIELD, CALIFORNIA 93303

rain for rent inc.
PHONE (805) 399-9124 TWX 910-327-1107 LAKECO

February 24, 1988

TO: Dr. Bill Frankenburger
Dept. of Soil
Ext. 3405

FROM: Dave Jones

Dear Bill:

As you have requested, the following number is a quotation for a second year rental on the pumps and irrigation pipe on the Kesterson project. We are unable to pass much savings back to you on a second year rental on the diesel pump due to the low original quote price and the fact that annual utilization of the pump at Kesterson would be far below our normal rental utilization. However, we are in a position to quote you a significantly reduced price on the rental of the lateral pipe, mainline pipe and sprinklers and risers. This second year price is not a price we could live with the first year. For your records the reduction in price represents the savings at our company in the following areas:

1. No rehandling of pipe at our facilities;

2. No reteating and inspection of the pipe following a one year return;

3. No remarketing costs for equipment;

4. No repairs that always result in the movement and storage of aluminum pipe;

5. No new administrative costs. ie: credit checks, rebilling activities or receivables administration

Now that you have a feel for the areas of cost reduction, we are prepared to state that we will pass all of these cost reduction on to the user for the second year at the total rental rate of $228,700.00 for the entire rental system on 500 acres. A rental system for the second year on all of Kesterson would be approximately $602,000.00.

We hope this will assist you in your project.

Best Regards,

Dave Jones

Dave Jones

P00001913